Ozone Depletion FAQ

Contents

Robert Parson's Ozone Depletion FAQ: Introductory Comments

Subject: Ozone Depletion FAQ Part I: The Stratosphere/The Ozone Layer.

Subject: Ozone Depletion FAQ Part II: Stratospheric Chlorine and Bromine

Subject: Ozone Depletion FAQ Part III: Antarctic

Subject: Ozone Depletion FAQ Part IV: UV Radiation and its Effects

Robert Parson's Ozone Depletion FAQ: Introductory Comments

Summary: This is the first of four files dealing with stratospheric
ozone depletion. It provides scientific background for
the more detailed questions in the other three parts.
Originator: rparson@rintintin.Colorado.EDU
Keywords: ozone layer cfc stratosphere depletion
Sender: usenet@cnsnews.Colorado.EDU (Net News Administrator)
Nntp-Posting-Host: rintintin.colorado.edu
Reply-To: rparson@rintintin.colorado.edu
Organization: University of Colorado, Boulder
Date: Fri, 25 Mar 1994 04:12:57 GMT
Approved: news-answers-request@MIT.Edu
Lines: 1001
Xref: news.Brown.EDU sci.environment:16913 sci.answers:1005 news.answers:16036

Archive-name: ozone-depletion/intro
Last-modified: 25 March 1994
Version: 4.2

These files are posted monthly, usually in the third week of the month.
They may be obtained by anonymous ftp from rtfm.mit.edu (18.70.0.209)
in the directory:

  /pub/usenet/news.answers/ozone-depletion

 which contains the four files intro, stratcl, antarctic, and uv.

 They may also be obtained by sending the following message
 to mail-server@rtfm.mit.edu:

  send usenet/news.answers/ozone-depletion/intro
  send usenet/news.answers/ozone-depletion/stratcl
  send usenet/news.answers/ozone-depletion/antarctic
  send usenet/news.answers/ozone-depletion/uv

 Leave the subject line blank.
 If you want to find out more about the mail server, send a
 message to it containing the word "help".

 ****

This is the first of four FAQ files dealing with stratospheric ozone
depletion. This part deals with basic scientific questions about the
ozone layer, and serves as an introduction to the remaining parts which
are more specialized. Part II deals with sources of stratospheric
chlorine and bromine, part III with the Antarctic Ozone Hole, and Part
IV with the properties and effects of ultraviolet radiation. The later
parts are mostly independent of each other, but they all refer back.
to Part I. I emphasize physical and chemical mechanisms
rather than biological effects, although I make a few remarks about
the latter in part IV. I have little to say about policy matters
other than a very brief summary at the end of part I.

The overall approach I take is conservative. I concentrate on what
is known and on most probable, rather than worst-case, scenarios.
For example, I have relatively little to say about the effects
of UV radiation on terrestrial plants - this does not mean that the
effects are small, it means that they are as yet not well
quantified (and moreover, I am not well qualified to interpret the
literature.) Policy decisions must take into account not only the
most probable scenario, but also a range of less probable ones.
There have been surprises, mostly unpleasant, in this field in the
past, and there are sure to be more in the future.

| Caveat: I am not a specialist. In fact, I am not an atmospheric

| chemist at all - I am a physical chemist studying gas-phase
| reactions who talks to atmospheric chemists. These files are an
| outgrowth of my own efforts to educate myself about this subject
| I have discussed some of these issues with specialists but I am
| solely responsible for everything written here, including all errors.
| This document should not be cited in publications off the net;
| rather, it should be used as a pointer to the published literature.

*** Corrections and comments are welcomed.

- Robert Parson
  Associate Professor
  Department of Chemistry and Biochemistry
  University of Colorado (for which I do not speak)

  rparson@rintintin.colorado.edu

Subject: Ozone Depletion FAQ Part I: The Stratosphere/The Ozone Layer.

CONTENTS

1. THE STRATOSPHERE

1.1) What is the stratosphere?

The stratosphere extends from about 15 km to 50 km. In the stratosphere temperature increases with altitude, due to the absorption of UV light by oxygen and ozone. This creates a global "inversion layer" which impedes vertical motion into and within the stratosphere - since warmer air lies above colder air, convection is inhibited. The word "stratosphere" is related to the word "stratification" or layering.

The stratosphere is often compared to the "troposphere", which is the atmosphere below about 15 km. The boundary - called the "tropopause" - between these regions is quite sharp, but its precise location varies between ~10 and ~17 km, depending upon latitude and season. The prefix "tropo" refers to change: the troposphere is the part of the atmosphere in which weather occurs. This results in relatively rapid mixing of tropospheric air. [Wayne] [Wallace and Hobbs]

Above the stratosphere lie the "mesosphere", ranging from ~50 to ~100 km, in which temperature decreases with altitude; the "thermosphere", ~100-400 km, in which temperature increases with altitude again, and the "exosphere", beyond ~400 km, which fades into the background of interplanetary space. In the upper mesosphere and thermosphere electrons and ions are abundant, so these regions are also referred to as the "ionosphere". In technical literature the term "lower atmosphere" is synonymous with the troposphere, "middle atmosphere" refers to the stratosphere and mesosphere, while "upper atmosphere" is usually reserved for the thermosphere and exosphere. This usage is not universal, however, and one occasionally sees the term "upper atmosphere" used to describe everything above the troposphere (for example, in NASA's Upper Atmosphere Research Satellite, UARS.)

1.2) How is the composition of air described?
   (What is a 'mixing ratio'?)

The density of the air in the atmosphere depends upon altitude, and in a complicated way because the temperature also varies with

altitude. It is therefore awkward to report concentrations of
atmospheric species in units like g/cc or molecules/cc. Instead,
it is convenient to report the "mole fraction", the relative
number of molecules of a given type in an air sample. Atmospheric
scientists usually call a mole fraction a "mixing ratio". Typical
units for mixing ratios are parts-per-million, billion, or
trillion by volume, designated as "ppmv", "ppbv", and "pptv"
respectively. (The expression "by volume" reflects Avogadro's Law -
for an ideal gas mixture, equal volumes contain equal numbers of
molecules - and serves to distinguish mixing ratios from "mass
fractions" which are given as parts-per-million by weight.) Thus
when it is said that the mixing ratio of hydrogen chloride at 3 km
is 0.1 ppbv, it means that 1 out of every 10 billion molecules in
an air sample collected at that altitude will be an HCl molecule.
[Wayne] [Graedel and Crutzen]

1.3) How does the composition of the atmosphere change with altitude?
   (Or, how can CFC's get up to the stratosphere when they are
     heavier than air?)

In the earth's troposphere and stratosphere, most stable chemical
species are "well-mixed" - their mixing ratios are independent of
altitude. If a species' mixing ratio changes with altitude, some
kind of physical or chemical transformation is taking place. That
last statement may seem surprising - one might expect the heavier
molecules to dominate at lower altitudes. The mixing ratio of
Krypton (mass 84), then, would decrease with altitude, while that
of Helium (mass 4) would increase. In reality, however, molecules
do not segregate by weight in the troposphere or stratosphere.
The relative proportions of Helium, Nitrogen, and Krypton are
unchanged up to about 100 km.

Why is this? Vertical transport in the troposphere takes place by
convection and turbulent mixing. In the stratosphere and in the
mesosphere, it takes place by "eddy diffusion" - the gradual mechanical
mixing of gas by motions on small scales. These mechanisms do not
distinguish molecular masses. Only at much higher altitudes do mean
free paths become so large that molecular diffusion dominates and
gravity is able to separate the different species, bringing hydrogen and
helium atoms to the top. [Wayne] [Wallace and Hobbs]

Experimental measurements of the fluorocarbon CF4 verify this homogeneous mixing. CF4 has an extremely long lifetime in the stratosphere - probably many thousands of years. The mixing ratio of CF4 in the stratosphere was found to be 0.056-0.060 ppbv from 10-50 km, with no overall trend. [Zander et al. 1992]

An important trace gas that is *not* well-mixed is water vapor. The lower troposphere contains a great deal of water - as much as 30,000 ppmv in humid tropical latitudes. High in the troposphere, however, the water condenses and falls to the earth as rain or snow, so that the stratosphere is extremely dry, typical mixing ratios being about 4 ppmv. Indeed, the transport of water vapor from troposphere to stratosphere is even more inefficient than this would suggest, since much of the small amount of water in the stratosphere is actually produced in situ by the oxidation of methane.

Sometimes that part of the atmosphere in which the chemical composition of stable species does not change with altitude is called the "homosphere". The homosphere includes the troposphere, stratosphere, and mesosphere. The upper regions of the atmosphere - the "thermosphere" and the "exosphere" - are then referred to as the "heterosphere". [Wayne] [Wallace and Hobbs]

2. THE OZONE LAYER

2.1) How is ozone created?

Ozone is formed naturally in the upper stratosphere by short wavelength ultraviolet radiation. Wavelengths less than ~240 nanometers are absorbed by oxygen molecules (O_2), which dissociate to give O atoms. The O atoms combine with other oxygen molecules to make ozone:

$O_2 + h\nu \rightarrow O + O$ (wavelength < 240 nm)
$O + O_2 \rightarrow O_3$
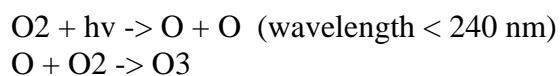
2.2) How much ozone is in the layer, and what is a "Dobson Unit" ?

A Dobson Unit (DU) is a convenient scale for measuring the total amount of ozone occupying a column overhead. If the ozone layer

over the US were compressed to 0 degrees Celsius and 1 atmosphere pressure, it would be about 3 mm thick. So, 0.01 mm thickness at 0 C and 1 at is defined to be 1 DU; this makes the ozone layer over the US come out to ~300 DU. In absolute terms, 1 DU is about 2.7×10^{16} molecules/cm^2.

In all, there are about 3 billion metric tons, or 3×10^{15} grams, of ozone in the earth's atmosphere; about 90% of this is in the stratosphere.

The unit is named after G.M.B. Dobson, who carried out pioneering studies of atmospheric ozone between ~1920-1960. Dobson designed the standard instrument used to measure ozone from the ground. The Dobson spectrometer measures the intensity solar UV radiation at four wavelengths, two of which are absorbed by ozone and two of which are not. These instruments are still in use in many places, although they are gradually being replaced by the more elaborate Brewer spectrometers. Today ozone is measured in many ways, from aircraft, balloons, satellites, and space shuttle missions, but the worldwide Dobson network is the only source of long-term data. A station at Arosa in Switzerland has been measuring ozone since the 1920's, and some other stations have records that go back nearly as long (although many were interrupted during World War II). The present worldwide network went into operation in 1956-57.

2.3) How is ozone distributed in the stratosphere?

In absolute terms: about 10^{12} molecules/cm^3 at 15 km, rising to nearly 10^{13} at 25 km, then falling to 10^{11} at 45 km.

In relative terms: ~0.5 parts per million by volume (ppmv) at 15 km, rising to ~8 ppmv at ~35 km, falling to ~3 ppmv at 45 km.

Even in the thickest part of the layer, ozone is a trace gas.

2.4) How does the ozone layer work?

UV light with wavelengths between 240 and 320 nm is absorbed by ozone, which then falls apart to give an O atom and an O2 molecule. The O atom soon encounters another O2 molecule, however (at all times, the concentration of O2 far exceeds that of O3), and recreates O3:

O3 + hv -> O2 + O
O + O2 -> O3
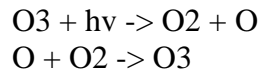
Thus ozone absorbs UV radiation without itself being consumed;
the net result is to convert UV light into heat. Indeed, this is
what causes the temperature of the stratosphere to increase with
altitude, giving rise to the inversion layer that traps molecules in
the troposphere. The ozone layer isn't just in the stratosphere; the
ozone layer is responsible for the existence of the stratosphere.

Ozone is destroyed if an O atom and an O3 molecule meet:

 O + O3 -> 2 O2 ("recombination").

This reaction is slow, however, and if it were the only mechanism
for ozone loss, the ozone layer would be about twice as thick
as it is. Certain trace species, such as the oxides of Nitrogen (NO
and NO2), Hydrogen (H, OH, and HO2) and chlorine (Cl, ClO and ClO2)
can catalyze the recombination. The present ozone layer is a
result of a competition between photolysis and recombination;
increasing the recombination rate, by increasing the
concentration of catalysts, results in a thinner ozone layer.
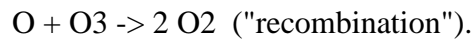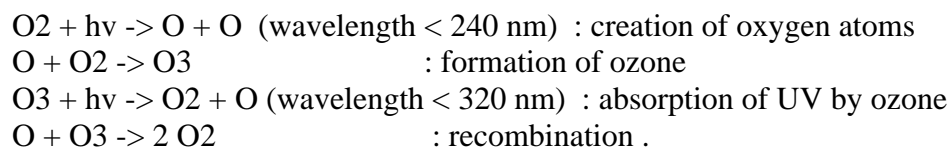
Putting the pieces together, we have the set of reactions proposed
in the 1930's by Sidney Chapman:

 O2 + hv -> O + O (wavelength < 240 nm) : creation of oxygen atoms
 O + O2 -> O3   : formation of ozone
 O3 + hv -> O2 + O (wavelength < 320 nm) : absorption of UV by ozone
 O + O3 -> 2 O2   : recombination .

Since the photolysis of O2 requires UV radiation while
recombination does not, one might guess that ozone should increase
during the day and decrease at night. This has led some people to
suggest that the "antarctic ozone hole" is merely a result of the
long antarctic winter nights. This inference is incorrect, because
the recombination reaction requires oxygen atoms which are also
produced by photolysis. Throughout the stratosphere the concentration
of O atoms is orders of magnitude smaller than the concentration of
O3 molecules, so both the production and the destruction of ozone by

the above mechanisms shut down at night. In fact, the thickness of the ozone layer varies very little from day to night, and above 70 km ozone concentrations actually increase at night.

(The unusual catalytic cycles that operate in the antarctic ozone hole do not require O atoms; however, they still require light to operate because they also include photolytic steps. See Part III.)

2.5) What sorts of natural variations does the ozone layer show?

There are substantial variations from place to place, and from season to season. There are smaller variations on time scales of years and more. [Wayne] [Rowland 1991]

 a. Regional and Seasonal Variation

Since solar radiation makes ozone, one expects to see the thickness of the ozone layer vary during the year. This is so, although the details do not depend simply upon the amount of solar radiation received at a given latitude and season - one must also take atmospheric motions into account. (Remember that both production and destruction of ozone require solar radiation.)

The ozone layer is thinnest in the tropics, about 260 DU, almost independent of season. Away from the tropics seasonal variations become important, but in no case (outside the Antarctic ozone hole) does the layer become appreciably thinner than in the tropics. For example:

Location	Column thickness, Dobson Units			
	Jan	Apr	Jul	Oct
Huancayo, Peru (12 degrees S) :	255	255	260	260
Aspendale, Australia (38 deg. S):	300	280	335	360
Arosa, Switzerland (47 deg. N):	335	375	320	280
St. Petersburg, Russia (60 deg. N):	360	425	345	300

These are monthly averages. Interannual standard deviations amount to ~5 DU for Huancayo, 25 DU for St. Petersburg. [Rowland 1991]. Notice that the highest ozone levels are found in the spring, not, as one might guess, in summer, and the lowest in the fall, not winter. Indeed, at high latitudes in the Northern Hemisphere there is more ozone in January than in July! Most of the ozone is created over the tropics, and then is carried to higher latitudes by prevailing winds (the general circulation of the stratosphere.) [Dobson] [Brasseur and Solomon]

The antarctic ozone hole, discussed in detail in Part III, falls *far outside* this range of natural variation. Mean October ozone at Halley Bay on the Antarctic coast was 117 DU in 1993, down from 321 DU in 1956.

b. Year-to-year variations.

Since ozone is created by solar UV radiation, one expects to see some correlation with the 11-year solar sunspot cycle. Higher sunspot activity corresponds to more solar UV and hence more rapid ozone production. This correlation has been verified, although its effect is small, about 2% from peak to trough averaged over the earth, about 4% in polar regions. [Stolarski et al.]

Another natural cycle is connected with the "quasibiennial oscillation", in which tropical winds in the lower stratosphere switch from easterly to westerly every 26 months. This leads to variations of the order of 3% at a given latitude, although the effect tends to cancel when one averages over the entire globe.

Episodes of unusual solar activity ("solar proton events") can also affect ozone levels, as can major volcanic eruptions such as Agung in 1963, El Chichon in 1982, and Pinatubo in 1991. (The principal mechanism for this is not injection of chlorine into the stratosphere, as discussed in Part II, but rather the injection of sulfate aerosols which change the radiation balance in the stratosphere by scattering light, and which convert inactive chlorine compounds to active, ozone-destroying forms.) These are all small effects, however, (a few % at most in a global average), and persist for short periods, 3 years or less.

2.6) What are CFC's?

CFC's - ChloroFluoroCarbons - are a class of volatile organic compounds that have been used as refrigerants, aerosol propellants, foam blowing agents, and as solvents in the electronic industry. They are chemically very unreactive, and hence safe to work with. In fact, they are so inert that the natural reagents that remove most atmospheric pollutants do not react with them, so after many years they drift up to the stratosphere where short-wave UV light dissociates them. CFC's were invented in 1928, but only came into large-scale production after ~1950. Since that year, the total amount of chlorine in the stratosphere has increased by a factor of 4. [Solomon]

The most important CFC's for ozone depletion are:

CF_2Cl_2 (CFC-12),
$CFCl_3$ (CFC-11), and
$CF_2ClCFCl_2$ (CFC-113).

In discussing ozone depletion, "CFC" is occasionally used to refer to a somewhat broader class of chlorine-containing organic compounds that have similar properties - unreactive in the troposphere, but readily photolyzed in the stratosphere. These include:

HydroChloroFluoroCarbons such as $CHClF_2$ (HCFC-22),
Carbon Tetrachloride, CCl_4,
Methyl Chloroform, CH_3CCl_3,
and Methyl Chloride, CH_3Cl.

(The more careful publications always use phrases like "CFC's and related compounds", but this gets tedious.)

Only methyl chloride has a large natural source; it is produced biologically in the oceans and chemically from biomass burning. The CFC's and CCl_4 are nearly inert in the troposphere, and have lifetimes of 50-200+ years. Their major "sink" is photolysis by UV radiation. [Rowland 1989, 1991] The hydrogen-containing halocarbons are more reactive, and are removed in the troposphere by reactions with OH radicals. This process is slow, however, and they live long

enough (1-20 years) for a large fraction to reach the stratosphere.

Most of Part II is devoted to stratospheric chlorine chemistry; look there for more detail.

2.7) How do CFC's destroy ozone?

CFC's themselves do not destroy ozone; certain of their decay products do. After CFC's are photolyzed, most of the chlorine eventually ends up as Hydrogen Chloride, HCl, or Chlorine Nitrate, ClONO2. These are called "reservoir species" - they do not themselves react with ozone. However, they do decompose to some extent, giving, among other things, a small amount of atomic chlorine, Cl, and Chlorine Monoxide, ClO, which can catalyze the destruction of ozone by a number of mechanisms. The simplest is:

Cl + O3 -> ClO + O2

ClO + O -> Cl + O2

Net effect: O3 + O -> 2 O2
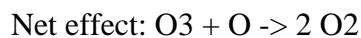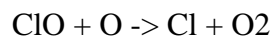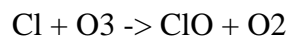
Note that the Cl atom is a catalyst - it is not consumed by the reaction. Each Cl atom introduced into the stratosphere can destroy thousands of ozone molecules before it is removed. The process is even more dramatic for Bromine - it has no stable "reservoirs", so the Br atom is always available to destroy ozone. On a per-atom basis, Br is 10-100 times as destructive as Cl. On the other hand, chlorine and bromine concentrations in the stratosphere are very small in absolute terms. The mixing ratio of chlorine from all sources in the stratosphere is about 3 parts per billion, (most of which is in the form of CFC's that have not yet fully decomposed) whereas ozone mixing ratios are measured in parts per million. Bromine concentrations are about 100 times smaller still. (See Part II.)

The complete chemistry is very complicated - more than 100 distinct species are involved. The rate of ozone destruction at any given time and place depends strongly upon how much Cl is present as Cl or ClO, and thus upon the rate at which Cl is released from its reservoirs. This makes quantitative predictions of future

ozone depletion difficult. [Rowland 1989, 1991] [Wayne]

2.8) What about HCFC's and HFC's? Do they destroy ozone?

HCFC's (hydrochlorofluorocarbons) differ from CFC's in that only
some, rather than all, of the hydrogen in the parent hydrocarbon
has been replaced by chlorine or fluorine. The most familiar
example is $CHClF_2$, known as "HCFC-22", used as a refrigerant and
in many home air conditioners (auto air conditioners use CFC-12).
The hydrogen atom makes the molecule susceptible to attack by the
hydroxyl (OH) radical, so a large fraction of the HCFC's are
destroyed before they reach the stratosphere. Molecule for
molecule, then, HCFC's destroy much less ozone than CFC's, and
they were suggested as CFC substitutes as long ago as 1976.

The impact of a compound on stratospheric ozone is usually
measured by its "ozone depletion potential", defined as the
steady-state limit of the amount of ozone destroyed by the
halocarbon, relative to the amount destroyed by CFC-12. HCFC's
generally have ozone depletion potentials around 0.01-0.1, so that
in the long time limit a typical HCFC will have destroyed 1-10% as
much ozone as the same amount of CFC-12. This measure can sometimes
be misleading, however. Since the HCFC's are more reactive in the
troposphere, fewer of them reach the stratosphere. However, they are
also more reactive in the stratosphere, so they release chlorine
more quickly. Just as short-lived radioisotopes are more intensely
radioactive than long-lived ones, those HCFC's that do reach the
stratosphere deplete ozone more quickly than CFC's. The short-term
effects are therefore larger than one would predict from the ozone
depletion potential alone, and the long-term effects correspondingly
smaller. This must be taken into account when substituting HCFC's
for CFC's. [Solomon and Albritton]

HFC's, hydrofluorocarbons, contain no chlorine at all, and hence
have an ozone depletion potential of zero. (In 1993 there were
tentative reports that the fluorocarbon radicals produced by
photolysis of HFC's could catalyze ozone loss, but this has now
been shown to be negligible [Ravishankara et al.]) A familiar
example is CF_3CH_2F, known as HFC-134a, which is being used in some
automobile air conditioners and refrigerators. HFC-134a is more
expensive and more difficult to work with than CFC's, and while it

has no effect on stratospheric ozone it is a greenhouse gas (though somewhat less potent than the CFC's). Some engineers have argued that non-CFC fluids, such as propane-isobutane mixtures, are better substitutes for CFC-12 in auto air conditioners than HFC-134a.

2.9) *IS* the ozone layer getting thinner (outside antarctica) ?

So it seems, although so far the effects are small. After carefully accounting for all of the known natural variations, a net decrease of about 3% per decade for the period 1978-1991 remains. This is a global average over latitudes from 66 degrees S to 66 degrees N (i.e. the arctic and antarctic are excluded in calculating the average). The depletion increases with latitude, being somewhat larger in the Southern Hemisphere. There is no significant depletion in the tropics; over the US, Europe, and Australia 4%/decade is typical. The depletion is larger in the winter months, smaller in the summer. [Stolarski et al.]

The following table, extracted from a much more detailed one in [Herman et al.], illustrates the seasonal and regional trends in percent per decade for the period 1979-1990:

Latitude	Jan	Apr	Jul	Oct	Example
65 N	-3.0	-6.6	-3.8	-5.6	Iceland
55 N	-4.6	-6.7	-3.1	-4.4	Moscow, Russia
45 N	-7.0	-6.8	-2.4	-3.1	Minneapolis, USA
35 N	-7.3	-4.7	-1.9	-1.6	Tokyo
25 N	-4.2	-2.9	-1.0	-0.8	Miami, FL, USA
5 N	-0.1	+1.0	-0.1	+1.3	Somalia
5 S	+0.2	+1.0	-0.2	+1.3	New Guinea
25 S	-2.1	-1.6	-1.6	-1.1	Pretoria, S.Africa
35 S	-3.6	-3.2	-4.5	-2.6	Buenos Aires
45 S	-4.8	-4.2	-7.7	-4.4	New Zealand
55 S	-6.1	-5.6	-9.8	-9.7	Tierra del Fuego
65 S	-6.0	-8.6	-13.1	-19.5	Palmer Peninsula

(These are longitudinally averaged satellite data, not individual measurements at the places listed in the right-hand column. There are longitudinal trends as well.)

Since 1991 these trends have accelerated. Satellite and
ground-based measurements now show a remarkable decline for 1992
and early 1993, a full 4% below the average value for the
preceding twelve years and 2-3% below the lowest values observed
in the earlier period. In Canada the spring ozone levels were 11-17%
below normal [Kerr et al.]. This decline overwhelms the
effect of the solar cycle; 1991 was a solar maximum, while the
1992 results are already below those for the 1986 solar minimum.
Sulfate aerosols from the July 1991 eruption of Mt. Pinatubo may
be the cause of this latest spike; these aerosols can convert
inactive "reservoir" chlorine into active ozone-destroying forms,
and can also interfere with the production and transport of ozone
by changing the solar radiation balance in the stratosphere.
[Brasseur and Granier] [Hofmann and Solomon] [Hofmann et al. 1994]
Another cause may be the unusually strong arctic polar vortex in
1992-93, which made the arctic stratosphere more like the antarctic
than is usually the case. [Gleason et al.] [Waters et al.]
Most likely all of these mechanisms are working in concert.

2.10) Is the middle-latitude ozone loss due to CFC emissions?

That's the majority opinion, although not everyone agrees. The
present trends are too small to allow a watertight case to be made
(as has been made for the far larger, but localized, depletion
in the Antarctic Ozone hole; see Part III.). Other possible causes
are being investigated. To quote from [WMO 1991], p. 4.1:

 *"The primary cause of the Antarctic ozone hole is firmly
established to be halogen chemistry....There is not a full
accounting of the observed downward trend in global ozone.
Plausible mechanisms include heterogeneous chemistry on sulfate
aerosols [which convert reservoir chlorine to active chlorine -
R.P.] and the transport of chemically perturbed polar air to middle
latitudes. Although other mechanisms cannot be ruled out, those
involving the catalytic destruction of ozone by chlorine and
bromine appear to be largely responsible for the ozone loss and
are the only ones for which direct evidence exists."*

 (emphases mine - RP)

The recent UARS measurements of ozone and ClO in the Northern
Hemisphere find a correlation between enhanced ClO and depleted
ozone, which further supports this hypothesis. [Waters et al.]
A legal analogy might be useful here - the connection between
antarctic ozone depletion and CFC emissions has been proved beyond
a reasonable doubt, while at middle latitudes there is only
probable cause for such a connection.

One must remember that there is a natural 10-20 year time lag
between CFC emissions and ozone depletion. Ozone depletion today is
(probably) due to CFC emissions in the '60's and '70's. Present
controls on CFC emissions are designed to avoid possibly large
amounts of ozone depletion 30 years from now, not to remediate the
depletion that has taken place up to now.

2.11) If the ozone is lost, won't the UV light just penetrate
      deeper into the atmosphere and make more ozone?

This does happen to some extent - it's called "self-healing" - and
has the effect of moving ozone from the upper to the lower
stratosphere. It is not a very effective stabilizing mechanism,
however. Recall that ozone is created by UV with wavelengths
less than 240 nm, but functions by absorbing UV with wavelengths
greater than 240 nm. The peak of the ozone absorption band is at
~250 nm, and the cross-section falls off at shorter wavelengths.
The O2 and O3 absorption bands do overlap, though, and UV radiation
between 200 and 240 nm has a good chance of being absorbed by
either O2 or O3. (Below 200 nm the O2 absorption cross-section
increases dramatically, and O3 absorption is insignificant in
comparison.) Since there is some overlap, a decrease in ozone does
lead to a small increase in absorption by O2. This is a weak feedback,
however, and it does not compensate for the ozone destroyed. Negative
feedback need not imply stability, just as positive feedback need not
imply instability.

Numerical calculations of ozone depletion take the "self-healing"
phenomenon into account, by letting the perturbed ozone layer come
into equilibrium with the exciting radiation. Even the simple
one-dimensional models used in the mid 1970's included this effect.

2.12) Do Space Shuttle launches damage the ozone layer?

No. In the early 1970's, when very little was known about the role of chlorine radicals in ozone depletion, it was suggested that HCl from solid-fueled rocket motors might have a significant effect upon the ozone layer - if not globally, perhaps in the immediate vicinity of the launch. It was quickly shown that the effect was negligible, and this has been repeatedly demonstrated since. Each shuttle launch produces about 68 metric tons of chlorine as HCl; a full year's worth of shuttle and solid-fueled rocket launches produces about 725 tons. This is negligible compared to chlorine emissions in the form of CFC's and related compounds (1.2 million tons/yr in the 1980's, of which ~0.3 million tons reach the stratosphere each year. It is also negligible in comparison to natural sources, which produce about 75,000 tons per year. [Prather et al.] [WMO 1991].

See also the sci.space FAQ, Part 10, "Controversial Questions".

2.13) Will commercial supersonic aircraft damage the ozone layer?

Short answer: Probably not. This problem is very complicated, and a definite answer will not be available for several years, but present model calculations indicate that a fleet of high-speed civil transports would deplete the ozone layer by < 1%. [WMO 1991]

Long answer (this is a tough one):

Supersonic aircraft fly in the stratosphere. Since vertical transport in the stratosphere is slow, the exhaust gases from a supersonic jet can stay there for two years or more. The most important exhaust gases are the nitrogen oxides, NO and NO2, collectively referred to as "NOx". NOx is produced from ordinary nitrogen and oxygen by electrical discharges (e.g. lightning) and by high-temperature combustion (e.g. in automobile and aircraft engines).

The relationship between NOx and ozone is complicated. In the troposphere, NOx makes ozone, a phenomenon well known to residents of Los Angeles and other cities beset by photochemical smog. At high altitudes in the troposphere, similar chemical reactions produce ozone as a byproduct of the oxidation of methane; for this reason ordinary subsonic aircraft actually increase the thickness of the ozone layer by a very small amount.

Things are very different in the stratosphere. Here the principal source of NOx is nitrous oxide, N2O ("laughing gas"). Most of the N2O in the atmosphere comes from bacteriological decomposition of organic matter - reduction of nitrate ions or oxidation of ammonium ions. (It was once assumed that anthropogenic sources were negligible in comparison, but this is now known to be false. The total anthropogenic contribution is now estimated at 8 Tg (teragrams)/yr, compared to a natural source of 18 Tg/yr. [Khalil and Rasmussen].) N2O, unlike NOx, is very unreactive - it has an atmospheric lifetime of more than 150 years - so it reaches the stratosphere, where most of it is converted to nitrogen and oxygen by UV photolysis. However, a small fraction of the N2O that reaches the stratosphere reacts instead with oxygen atoms (to be precise, with the very rare electronically excited singlet-D oxygen atoms), and this is the major natural source of NOx in the stratosphere. About 1.2 million tons are produced each year in this way. This source strength would be matched by 500 of the SST's designed by Boeing in the late 1960's, each spending 5 hours per day in the stratosphere. (Boeing was intending to sell 800 of these aircraft.) The Concorde, a slower plane, produces less than half as much NOx and flies at a lower altitude; since the Concorde fleet is small, its contribution to stratospheric NOx is not significant. Before sending large fleets of high-speed aircraft into the stratosphere, however, one should certainly consider the possible effects of increasing the rate of production of an important stratospheric trace gas by as much as a factor of two. [CIC 1975]

(Aside: subsonic aircraft do sometimes enter the stratosphere; however they stay very low and do not appreciably affect its chemistry.)

In 1969, Paul Crutzen discovered that NOx could be an efficient catalyst for the destruction of stratospheric ozone:

    NO + O3 -> NO2 + O2
    NO2 + O -> NO + O2
----
 net: O3 + O -> 2 O2
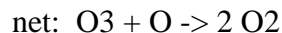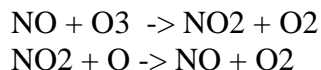
This sequence was rediscovered two years later by H. S. Johnston, who made the connection to SST emissions. Until then it had been thought that the radicals H, OH, and HO2 (referred to collectively as "HOx")

were the principal catalysts for ozone loss; thus, investigations of the impact of aircraft exhaust on stratospheric ozone had focussed on emissions of water vapor, a possible source for these radicals. (The importance of chlorine radicals, Cl, ClO, and ClO2, referred to as - you guessed it - "ClOx", was not discovered until 1973.) It had been argued - correctly, as it turns out - that water vapor injection was unimportant for determining the ozone balance. The discovery of the NOx cycle threw the question open again.

Beginning in 1972, the U.S. National Academies of Science and Engineering and the Department of Transportation sponsored an intensive program of stratospheric research. [CIC 1975] It soon became clear that the relationship between NOx emissions and the ozone layer was very complicated. The stratospheric lifetime of NOx is comparable to the timescale for transport from North to South, so its concentration depends strongly upon latitude. Much of the NOx is injected near the tropopause, a region where quantitative modelling is very difficult, and the results of calculations depend sensitively upon how troposphere-stratosphere exchange is treated. Stratospheric NOx chemistry is extremely complicated, much worse than chlorine chemistry. Among other things, NO2 reacts rapidly with ClO, forming the inactive chlorine reservoir ClONO2 - so while on the one hand increasing NOx leads directly to ozone loss, on the other it suppresses the action of the more potent chlorine catalyst. And on top of all of this, the SST's always spend part of their time in the troposphere, where NOx emissions cause ozone increases. Estimates of long-term ozone changes due to large-scale NOx emissions varied markedly from year to year, going from -10% in 1974, to +2% (i.e. a net ozone gain) in 1979, to -8% in 1982. (In contrast, while the estimates of the effects of CFC emissions on ozone also varied a great deal in these early years, they always gave a net loss of ozone.) [Wayne]

The discovery of the Antarctic ozone hole added a new piece to the puzzle. As described in Part III, the ozone hole is caused by heterogeneous chemistry on the surfaces of stratospheric cloud particles. While these clouds are only found in polar regions, similar chemical reactions take place on sulfate aerosols which are found throughout the lower stratosphere. The most important of the aerosol reactions is the conversion of N2O5 to nitric acid:

N2O5 + H2O -> 2 HNO3 (catalyzed by aerosol surfaces)

N2O5 is in equilibrium with NOx, so removal of N2O5 by this reaction lowers the NOx concentration. The result is that in the lower stratosphere the NOx catalytic cycle contributes much less to overall ozone loss than the HOx and ClOx cycles. Ironically, the same processes that makes chlorine-catalyzed ozone depletion so much more important than was believed 10 years ago, also make NOx-catalyzed ozone loss less important.

In the meantime, there has been a great deal of progress in developing jet engines that will produce much less NOx - up to a factor of 10 - than the old Boeing SST. The most recent model calculations indicate that a fleet of the new "high-speed civil transports" would deplete the ozone layer by less than 1%. Caution is still required, since the experiment has not been done - we have not yet tried adding large amounts of NOx to the stratosphere. The forecasts, however, are good. [WMO 1991, Ch. 10]

....
Aside: One sometimes hears that the US government killed the SST project in 1971 because of concerns raised by H. S. Johnston's work on NOx. This is not true. The US House of Representatives had already voted to cut off Federal funding for the SST when Johnston began his calculations. The House debate had centered around economics and the effects of noise, especially sonic booms, although there were some vague remarks about "pollution" and one physicist had testified about the possible effects of water vapor on ozone. About 6 weeks after both houses had voted to cancel the SST, its supporters succeeded in reviving the project in the House. In the meantime, Johnston had sent a preliminary report to several professional colleagues and submitted a paper to Science. A preprint of Johnston's report leaked to a small California newspaper which published a highly sensationalized account. The story hit the press a few days before the Senate voted, 58-37, not to revive the SST. (The previous Senate vote had been 51-46 to cancel the project. The reason for the larger majority in the second vote was probably the statement by Boeing's chairman that at least $500 million more would be needed to revive the program.)
....

2.14) What is being done about ozone depletion?

The 1987 Montreal Protocol specified that CFC emissions should be reduced by 50% by the year 2000 (they had been increasing by 3% per year.) This agreement was amended in London in 1990, to state that production of CFC's, CCl4, and halons should cease entirely by the year 2000. Restrictions have also been applied to other Cl sources such as methylchloroform. (The details of the protocols are complicated, involving different schedules for different compounds, delays for developing nations, etc. See the book by [Benedick].) The phase-out schedule was accelerated by four years by the 1992 Copenhagen agreements. A great deal of effort has been devoted to recovering and recycling CFC's that are currently being used in closed-cycle systems.

Recent NOAA measurements [Elkins et al.] show that the rate of increase of halocarbon concentrations in the atmosphere has decreased markedly since 1987, by a factor of 4 for CFC-11 and a factor of 2 for CFC-12. It appears that the Protocols are being observed. Under these conditions total stratospheric chlorine is predicted to peak in the first decade of the 21st century, and to slowly decline thereafter.

Model calculations predict that ozone levels, averaged over the year and over the Northern hemisphere, will fall to about 4% below 1980 levels in the first decade of the 21st century if the protocols are obeyed. Very little depletion is expected in the tropics, so correspondingly larger losses - more than 6% - are expected at middle and high latitudes. These same models have systematically underestimated ozone depletion in the past, so significantly larger losses are expected. In fact, 4% global year-averaged ozone depletion was already measured in 1993 [Gleason et al.] although this may be a transient caused by Mt. Pinatubo's eruption in July 1991. After 2010 the ozone layer will slowly recover over a period of 20 years or so, although the form of the recovery is strongly model-dependent. [WMO 1991] I have no results at hand for the southern hemisphere; if current trends continue ozone depletion will be more serious there. The antarctic ozone hole is expected to last until 2050 or so. This does not take into account the possibility of global warming,

which by cooling the stratosphere could make ozone depletion more serious both at mid latitudes and in polar regions.

Some scientists are investigating ways to replenish stratospheric ozone, either by removing CFC's from the troposphere or by tying up the chlorine in inactive compounds. This is discussed in Part III.

3. REFERENCES FOR PART I

A remark on references: they are neither representative nor comprehensive. There are hundreds of people working on these problems. Where possible I have limited myself to papers that are (1) available outside of University libraries (e.g. Science or Nature rather than archival journals such as J. Geophys. Res.) and (2) directly related to the "frequently asked questions". I have not listed papers whose importance is primarily historical. Readers who want to see "who did what" should consult the review articles listed below, or, if they can get them, the WMO reports which are extensively documented.

Introductory Reading:

[Graedel and Crutzen] T. E. Graedel and P. J. Crutzen, Atmospheric Change: an Earth System Perspective, Freeman, NY 1993.

[Rowland 1989] F.S. Rowland, "Chlorofluorocarbons and the depletion of stratospheric ozone", American Scientist 77, 36, 1989.

[Zurer] P. S. Zurer, "Ozone Depletion's Recurring Surprises Challenge Atmospheric Scientists", Chemical and Engineering News, 24 May 1993, pp. 9-18.

Books and Review Articles:

[Benedick] R. Benedick, Ozone Diplomacy, Harvard, 1991.

[Brasseur and Solomon] G. Brasseur and S. Solomon, Aeronomy of

the Middle Atmosphere, 2nd. Edition, D. Reidel, 1986

[Dobson] G.M.B. Dobson, Exploring the Atmosphere, 2nd Edition,
 Oxford, 1968.

[CIC 1975] Climate Impact Committee, National Research Council,
Environmental Impact of Stratospheric Flight, National Academy of
Sciences, 1975.

[Johnston 1992] H. S. Johnston, "Atmospheric Ozone",
Annu. Rev. Phys. Chem. 43, 1, 1992.

[McElroy and Salawich] M. McElroy and R. Salawich,
"Changing Composition of the Global Stratosphere",
Science 243, 763, 1989.

[Rowland 1991] F. S. Rowland, "Stratospheric Ozone Depletion",
Ann. Rev. Phys. Chem. 42, 731, 1991.

[Solomon] S. Solomon, "Progress towards a quantitative understanding
 of Antarctic ozone depletion", Nature 347, 347, 1990.

[Wallace and Hobbs] J. M. Wallace and P. V. Hobbs,
Atmospheric Science: an Introductory Survey, Academic Press, 1977.

[Wayne] R. P. Wayne, Chemistry of Atmospheres,
     2nd. Ed., Oxford, 1991.

[WMO 1988] World Meteorological Organization,
Report of the International Ozone Trends Panel,
 Global Ozone Research and Monitoring Project - Report #18.

[WMO 1989] World Meteorological Organization,
Scientific Assessment of Stratospheric Ozone: 1991
 Global Ozone Research and Monitoring Project - Report #20.

[WMO 1991] World Meteorological Organization,
Scientific Assessment of Ozone Depletion: 1991
 Global Ozone Research and Monitoring Project - Report #25.

More Specialized:

[Brasseur and Granier] G. Brasseur and C. Granier, "Mt. Pinatubo
 aerosols, chlorofluorocarbons, and ozone depletion", Science
 257, 1239,1992.

[Elkins et al.] J. W. Elkins, T. M. Thompson, T. H. Swanson,
J. H. Butler, B. D. Hall, S. O. Cummings, D. A. Fisher, and
A. G. Raffo, "Decrease in Growth Rates of Atmospheric
Chlorofluorocarbons 11 and 12", Nature 364, 780, 1993.

[Gleason et al.] J. Gleason, P. Bhatia, J. Herman, R. McPeters, P.
Newman, R. Stolarski, L. Flynn, G. Labow, D. Larko, C. Seftor, C.
Wellemeyer, W. Komhyr, A. Miller, and W. Planet, "Record Low Global
Ozone in 1992", Science 260, 523, 1993.

[Herman et al.] J. R. Herman, R. McPeters, and D. Larko,
 "Ozone depletion at northern and southern latitudes derived
 from January 1979 to December 1991 TOMS data",
 J. Geophys. Res. 98, 12783, 1993.

[Hofmann and Solomon] D. J. Hofmann and S. Solomon, "Ozone
destruction through heterogeneous chemistry following the
eruption of El Chichon", J. Geophys. Res. 94, 5029, 1989.

[Hofmann et al. 1994] D. J. Hofmann, S. J. Oltmans, W. D. Komhyr,
J. M. Harris, J. A. Lathrop, A. O. Langford, T. Deshler,
B. J. Johnson, A. Torres, and W. A. Matthews,
"Ozone Loss in the lower stratosphere over the United States in
1992-1993: Evidence for heterogeneous chemistry on the Pinatubo
aerosol", Geophys. Res. Lett. 21, 65, 1994.

[Kerr et al.] J. B. Kerr, D. I. Wardle, and P. W. Towsick,
"Record low ozone values over Canada in early 1993",
Geophys. Res. Lett. 20, 1979, 1993.

[Khalil and Rasmussen] M.A.K. Khalil and R. Rasmussen, "The Global
 Sources of Nitrous Oxide", J. Geophys. Res. 97, 14651, 1992.

[Prather et al.] M. J. Prather, M.M. Garcia, A.R. Douglass, C.H.
Jackman, M.K.W. Ko, and N.D. Sze, "The Space Shuttle's impact on

the stratosphere", J. Geophys. Res. 95, 18583, 1990.

[Ravishankara et al.] A. R. Ravishankara, A. A. Turnipseed,
N. R. Jensen, S. Barone, M. Mills, C. J. Howard, and S. Solomon,
"Do Hydrofluorocarbons Destroy Stratospheric Ozone?",
 Science 263, 71, 1994.

[Solomon and Albritton] S. Solomon and D.L. Albritton,
"Time-dependent ozone depletion potentials for short- and long-term
forecasts", Nature 357, 33, 1992.

[Stolarski et al.] R. Stolarski, R. Bojkov, L. Bishop, C. Zerefos,
 J. Staehelin, and J. Zawodny, "Measured Trends in Stratospheric
Ozone", Science 256, 342 (17 April 1992)

[Waters et al.] J. Waters, L. Froidevaux, W. Read, G. Manney, L.
Elson, D. Flower, R. Jarnot, and R. Harwood, "Stratospheric ClO and
ozone from the Microwave Limb Sounder on the Upper Atmosphere
Research Satellite", Nature 362, 597, 1993.

[Zander et al. 1992] R. Zander, M. R. Gunson, C. B. Farmer, C. P.
Rinsland, F. W. Irion, and E. Mahieu, "The 1985 chlorine and
fluorine inventories in the stratosphere based on ATMOS
observations at 30 degrees North latitude", J. Atmos. Chem. 15,
171, 1992.

Subject: Ozone Depletion FAQ Part II: Stratospheric Chlorine and Bromine

This part deals not with ozone depletion per se (that is covered
in Part I) but rather with the sources and sinks of chlorine and
bromine in the stratosphere. Special attention is devoted to the
evidence that most of the chlorine comes from the photolysis of
CFC's and related compounds. Instead of relying upon qualitative
statements about relative lifetimes, solubilities, and so forth, I
have tried to give a sense of the actual magnitudes involved.
Fundamentally, this Part of the FAQ is about measurements, and I
have therefore included some tables to illustrate trends; the
data that I reproduce is in all cases a small fraction of what
has actually been published. In the first section I state the
present assessment of stratospheric chlorine sources and trends,
and then in the next section I discuss the evidence that leads to
those conclusions. After a brief discussion of Bromine in section 3,
I answer the most familiar challenges that have been raised in
section 4. Only these last are actually "Frequently Asked Questions";
however I have found the Question/Answer format to be useful
in clarifying the issues in my mind even when the questions are
rhetorical, so I have kept to it.

| Caveat: I am not a specialist. In fact, I am not an atmospheric
| chemist at all - I am a physical chemist studying gas-phase
| processes who talks to atmospheric chemists. These files are an
| outgrowth of my own efforts to educate myself about this subject.
| I have discussed some of these issues with specialists but I am
| solely responsible for everything written here, especially errors.

*** Corrections and comments are welcomed.

- Robert Parson
  Associate Professor
  Department of Chemistry and Biochemistry,
  University of Colorado (for which I do not speak)

  rparson@rintintin.colorado.edu

CONTENTS

==

1. CHLORINE IN THE STRATOSPHERE - OVERVIEW

1.1) Where does the Chlorine in the stratosphere come from?

~80% from CFC's and related manmade organic chlorine compounds,
 such as carbon tetrachloride and methyl chloroform

~15-20% from methyl chloride (CH3Cl), most of which is natural.

 A few % from inorganic sources, including volcanic eruptions.

 [WMO 1991] [Solomon] [AASE] [Rowland 1989,1991] [Wayne]

These estimates are based upon 20 years' worth of measurements of
organic and inorganic chlorine-containing compounds in the earth's
troposphere and stratosphere. Particularly informative is the
dependence of these compounds' concentrations on altitude and
their increase with time. The evidence is summarized in section 2
of this FAQ.

1.2) How has stratospheric chlorine changed with time?

The total amount of chlorine in the stratosphere has increased by
a factor of 2.5 since 1975 [Solomon] During this time period the
known natural sources have shown no major increases. On the other
hand, emissions of CFC's and related manmade compounds have
increased dramatically, reaching a peak in 1987. Extrapolating
back, one infers that total stratospheric chlorine has increased
by a factor of 4 since 1950.

1.3) How will stratospheric chlorine change in the future?

Since the 1987 Montreal Protocol (see Part I) production of
CFC's and related compounds has been decreasing rapidly. While
CFC concentrations are still increasing, the rate of increase
has diminished:

Growth Rate, pptv/yr   (From [Elkins et al.])

Year	CFC-12	CFC-11
1977-84	17	9
1985-88	19.5	11
1993	10.5	2.7

If this trend continues CFC concentrations in the troposphere will peak before the end of the century. The time scale for mixing tropospheric and lower stratospheric air is about 5 years, so stratospheric chlorine is expected to peak in the next decade and then slowly decline on a time scale of about 50 years.

2. THE CHLORINE CYCLE

2.1) What are the sources of chlorine in the troposphere?

Let us divide the chlorine-containing compounds found in the atmosphere into two groups, "organic chlorine" and "inorganic chlorine". The most important inorganic chlorine compound in the troposphere is hydrogen chloride, HCl. Its principal source is acidification of salt spray - reaction of atmospheric sulfuric and nitric acids with chloride ions in aerosols. At sea level, this leads to an HCl mixing ratio of 0.05 - 0.45 ppbv, depending strongly upon location (e.g. smaller values over land.) However, HCl dissolves very readily in water (giving hydrochloric acid), and condensation of water vapor efficiently removes HCl from the upper troposphere. Measurements show that the HCl mixing ratio is less than 0.1 ppbv at elevations above 7 km, and less than 0.04 ppbv at 13.7 km. [Vierkorn-Rudolf et al.] [Harris et al.]

There are many volatile organic compounds containing chlorine, but most of them are quickly decomposed by the natural oxidants in the troposphere, and the chlorine atoms that were in these compounds eventually find their way into HCl or other soluble species and are rained out. The most important exceptions are:

 ChloroFluoroCarbons, of which the most important are
 CF_2Cl_2 (CFC-12), $CFCl_3$ (CFC-11), and $CF_2ClCFCl_2$ (CFC-113);

HydroChloroFluoroCarbons such as CHClF2 (HCFC-22);

Carbon Tetrachloride, CCl4;

Methyl Chloroform, CH3CCl3;

and Methyl Chloride, CH3Cl (also called Chloromethane).

Only the last has a large natural source; it is produced
biologically in the oceans and chemically from biomass burning.
The CFC's and CCl4 are nearly inert in the troposphere, and have
lifetimes of 50-200+ years. Their major "sink" is photolysis by UV
radiation. [Rowland 1989, 1991] The hydrogen-containing halocarbons
are more reactive, and are removed in the troposphere by reactions
with OH radicals. This process is slow, however, and they live long
enough (1-20 years) for a large fraction to reach the stratosphere.

As a result of this enormous difference in atmospheric lifetimes,
there is more chlorine present in the lower atmosphere in
halocarbons than in HCl, even though HCl is produced in much larger
quantities. Total tropospheric organic chlorine amounted to
~3.8 ppbv in 1989 [WMO 1991], and this mixing ratio is very nearly
independent of altitude throughout the troposphere. Methyl Chloride,
the only ozone-depleting chlorocarbon with a major natural source,
makes up 0.6 ppbv of this total. Compare this to the tropospheric HCl
mixing ratios given above: < 0.5 ppbv at sea level, < 0.1 ppbv at 3 km,
and < 0.04 ppbv at 10 km.

2.2) In what molecules is stratospheric chlorine found?

The halocarbons described above are all found in the stratosphere,
and in the lower stratosphere they are the dominant form of chlorine.
At higher altitudes inorganic chlorine is abundant, most of it in
the form of HCl or of chlorine nitrate, ClONO2. These are called
"chlorine reservoirs"; they do not themselves react with ozone, but
they generate a small amount of chlorine-containing radicals - Cl,
ClO, ClO2, and related species, referred to collecively as the
"ClOx family" - which do. An increase in the concentration of
chlorine reservoirs leads to an increase in the concentration of
the ozone-destroying radicals.

2.3) What happens to organic chlorine in the stratosphere?

The organic chlorine compounds are dissociated by UV radiation having wavelengths near 230 nm. Since these wavelengths are also absorbed by oxygen and ozone, the organic compounds have to rise high in the stratosphere in order for this photolysis to take place. The initial (or, as chemists say, "nascent") products are a free chlorine atom and an organic radical, for example:

$CFCl_3 + hv \rightarrow CFCl_2 + Cl$
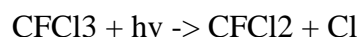
The chlorine atom can react with methane to give HCl and a methyl radical:

$Cl + CH_4 \rightarrow HCl + CH_3$
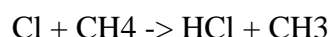
Alternatively, it can react with ozone and nitrogen oxides:

$Cl + O_3 \rightarrow ClO + O_2$
$ClO + NO_2 \rightarrow ClONO_2$
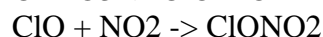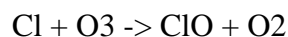
(There are other pathways, but these are the most important.)

The other nascent product ($CFCl_2$ in the above example) undergoes a complicated sequence of reactions that also eventually leads to HCl and $ClONO_2$. Most of the inorganic chlorine in the stratosphere therefore resides in one of these two "reservoirs". The immediate cause of the Antarctic ozone hole is an unusual sequence of reactions, catalyzed by polar stratospheric clouds, that "empty" these reservoirs and produce high concentrations of ozone-destroying ClO_x radicals. [Wayne] [Rowland 1989, 1991]

2.4) How do we know that CFC's are photolyzed in the stratosphere?

The UV photolysis cross-sections for the halocarbons have been measured in the laboratory; these tell us how rapidly they will dissociate when exposed to light of a given wavelength and intensity. We can combine this with the measured intensity of radiation in the stratosphere and deduce the way in which the mixing ratio of a given halocarbon should depend upon altitude. Since there is almost

no 230 nm radiation in the troposphere or in the lowest parts of the stratosphere, the mixing ratio should be independent of altitude there. In the middle stratosphere the mixing ratio should drop off quickly, at a rate which is determined by the photolysis cross-section. Thus each halocarbon has a characteristic "signature" in its mixing ratio profile, which can be calculated. Such calculations (first carried out in the mid 1970's) agree well with the distributions presented in the next section.

There is direct evidence as well. Photolysis removes a chlorine atom, leaving behind a reactive halocarbon radical. The most likely fate of this radical is reaction with oxygen, which starts a long chain of reactions that eventually remove all the chlorine and fluorine. Most of the intermediates are reactive free radicals, but two of them, COF2 and COFCl, are fairly stable (they are analogs of formaldehyde, H2CO) and live long enough to be detected. They have been found, at precisely those altitudes at which the CFC mixing ratios are dropping off rapidly (see below).

2.5) How is chlorine removed from the stratosphere?

Since the stratosphere is very dry, water-soluble compounds are not quickly washed out as they are in the troposphere. The stratospheric lifetime of HCl is about 2 years; the principal sink is transport back down to the troposphere.

2.6) How is chlorine distributed in the stratosphere?

Over the past 20 years an enormous effort has been devoted to identifying sources and sinks of stratospheric chlorine. The concentrations of the major species have been measured as a function of altitude, by "in-situ" methods (e.g. collection filters carried on planes and balloons) and by spectroscopic observations from aircraft, balloons, satellites, and the Space Shuttle. From all this work we now have a clear and consistent picture of the processes that carry chlorine through the stratosphere.

Let us begin by asking where inorganic chlorine is found. In the troposphere, the HCl mixing ratio decreased markedly with increasing altitude. In the stratosphere, on the other hand, it increases with altitude, rapidly up to about 35 km, and then more slowly up to 55km

and beyond. This was noticed as early as 1976 [Farmer et al.]
[Eyre and Roscoe] and has been confirmed repeatedly since. Chlorine
Nitrate (ClONO2), the other important inorganic chlorine compound in
the stratosphere, also increases rapidly in the lower stratosphere, and
then falls off at higher altitudes. These results strongly suggest
that HCl in the stratosphere is being produced there, not drifting
up from below.

Let us now look at the organic source gases. Here, the data show
that the mixing ratios of the CFC's and CCl4 are nearly independent
of altitude in the troposphere, and decrease rapidly with altitude
in the stratosphere. The mixing ratios of the more reactive
hydrogenated compounds such as CH3CCl3 and CH3Cl drop off somewhat
in the troposphere, but also show a much more rapid decrease in
the stratosphere. The turnover in organic chlorine correlates
nicely with the increase in inorganic chlorine, confirming the
hypothesis that CFC's are being photolyzed as they rise high enough
in the stratosphere to experience enough short-wavelength UV. At
the bottom of the stratosphere almost all of the chlorine is
organic, and at the top it is all inorganic. [Fabian et al.]
[Zander et al. 1987] [Zander et al. 1992] [Penkett et al.]

Finally, there are the stable reaction intermediates, COFCl and
COF2. These show up in the middle stratosphere, exactly where one
expects to find them if they are produced from organic source gases
and eventually react to give inorganic chlorine.

For example, the following is extracted from Tables II and III of
[Zander et al. 1992]; they refer to 30 degrees N Latitude in 1985.
I have rearranged the tables and rounded some of the numbers, and
the arithmetic in the second table is my own.

Organic Chlorine and Intermediates, Mixing ratios in ppbv

Alt., km	CH3Cl	CCl4	CCl2F2	CCl3F	CHClF2	CH3CCl3	C2F3Cl3	‖	COFCl
12.5	.580	.100	.310	.205	.066	.096	.021	‖	.004
15	.515	.085	.313	.190	.066	.084	.019	‖	.010
20	.350	.035	.300	.137	.061	.047	.013	‖	.035
25	.120	-	.175	.028	.053	.002	.004	‖	.077
30	-	-	.030	-	.042	-	-	‖	.029

```
40   -   -   -   -   -   -   -   || -
```

Inorganic Chlorine and Totals, Mixing ratios in ppbv

Alt.,	HCl	ClONO2	ClO	HOCl	||	Total Cl, Inorganic	Total Cl, Organic	Total Cl
km					||			
12.5	-	-	-	-	||	-	2.63	2.63
15	.065	-	-	-	||	0.065	2.50	2.56
20	.566	.212	-	-	||	0.778	1.78	2.56
25	1.027	.849	.028	.032	||	1.936	0.702	2.64
30	1.452	1.016	.107	.077	||	2.652	0.131	2.78
40	2.213	0.010	.234	.142	||	2.607	-	2.61

(I have included the intermediate COFCl in the Total Organic column.)

This is just an excerpt. The original tables give results every 2.5km from 12.5 to 55km, together with a similar inventory for Fluorine. Standard errors on total Cl were estimated to be 0.02-0.04 ppbv.

Notice that the total chlorine at any altitude is nearly constant at ~2.5-2.8 ppbv. This is what we would expect if the sequence of reactions that leads from organic sources to inorganic reservoirs was fast compared to vertical transport. Our picture, then, would be of a swarm of organic chlorine molecules slowly spreading upwards through the stratosphere, being converted into inorganic reservoir molecules as they climb. In fact this oversimplifies things - photolysis pops off a single Cl atom which does reach its final destination quickly, but the remaining Cl atoms are removed by a sequence of slower reactions. Some of these reactions involve compounds, such as NOx, which are not well-mixed; moreover, "horizontal" transport does not really take place along surfaces of constant altitude, so chemistry and atmospheric dynamics are in fact coupled together in a complicated way. These are the sorts of issues that are addressed in atmospheric models. Nevertheless, this simple picture helps us to understand the qualitative trends, and quantitative models confirm the conclusions [McElroy and Salawich].

We conclude that most of the inorganic chlorine in the stratosphere is produced there, as the end product of photolysis of the organic

chlorine compounds.

2.7) What happens to the Fluorine from the CFC's?

Most of it ends up as Hydrogen Fluoride, HF. The total amount of HF in the stratosphere increased by a factor of 3-4 between 1978 and 1989 [Zander et al., 1990] [Rinsland et al.]; the relative increase is larger for HF than for HCl (a factor of 2.2 over the same period) because the natural source, and hence the baseline concentration, is much smaller. For the same reason, the ratio of HF to HCl has increased, from 0.14 in 1977 to 0.23 in 1990. The fluorine budget, as a function of altitude, adds up in much the same way as the chlorine budget. [Zander et al. 1992].
There are some discrepancies in the lower stratosphere; model calculations predict less HF than is actually observed.

2.8) Summary of the Evidence

a. Inorganic chlorine, primarily of natural origin, is efficiently removed from the troposphere; organic chlorine, primarily anthropogenic, is not, and in the upper troposphere organic chlorine dominates overwhelmingly.

b. In the stratosphere, organic chlorine decreases with altitude, since at higher altitudes there is more short-wave UV available to photolyze it. Inorganic chlorine increases with altitude. At the bottom of the stratosphere essentially all of the chlorine is organic, at the top it is all inorganic, and reaction intermediates are found at intermediate altitudes.

c. Both HCl and HF in the stratosphere have been increasing steadily, in a correlated fashion, since they were first measured in the 1970's.

3. BROMINE

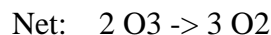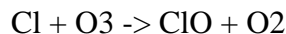3.1) Is bromine important to the ozone destruction process?

Br is present in much smaller quantities than Cl, but it is much more destructive on a per-atom basis. There is a large

natural source; manmade compounds contribute about 40% of the total.

3.2) How does bromine affect ozone?

Bromine concentrations in the stratosphere are ~150 times smaller
than chlorine concentrations. However, atom-for-atom Br is 10-100
times as effective as Cl in destroying ozone. (The reason for this
is that there is no stable 'reservoir' for Br in the stratosphere
- HBr and BrONO2 are very easily photolyzed so that nearly all of
the Br is in a form that can react with ozone. Contrariwise, F is
innocuous in the stratosphere because its reservoir, HF, is
extremely stable.) So, while Br is less important than Cl, it must
still be taken into account. Interestingly, the principal
pathway by which Br destroys ozone also involves Cl:

```
   BrO + ClO -> Br + Cl + O2
   Br + O3 -> BrO + O2
   Cl + O3 -> ClO + O2
  ----------------------------------
   Net:   2 O3 -> 3 O2
```
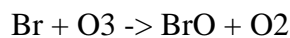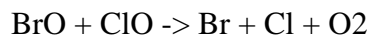
[Wayne p. 164] [Solomon]

so reducing stratospheric chlorine concentrations will, as a
side-effect, slow down the bromine pathways as well.

3.3) Where does the bromine come from?

The largest source of stratospheric Bromine is methyl bromide,
CH3Br. Much of this is naturally produced in the oceans and in
wildfires [Mano and Andreae], but 30 - 60% is manmade [Khalil et al.]
It is widely used as a fumigant.

Another important source is the family of "halons", widely used in fire
extinguishers. Like CFC's these compounds have long atmospheric
lifetimes (72 years for CF3Br) and very little is lost in the
troposphere. [Wayne p. 167]. At the bottom of the stratosphere
the total Br mixing ratio is ~20 parts-per-trillion (pptv), of which ~
8 pptv is manmade. [AASE] Uncertainties in these numbers are relatively
larger than for Cl, because the absolute quantities are so much smaller,

and we should expect to see these estimates change. Halons have been restricted under the Montreal Protocol, and regulations on methyl bromide use are under consideration.

4. COMMONLY ENCOUNTERED OBJECTIONS

4.1) CFC's are 4-8 times heavier than air, so how can they reach the stratosphere?

This is answered in Part I of this FAQ, section 1.3. Briefly, atmospheric gases do not segragate by weight in the troposphere and the stratosphere, because the mixing mechanisms (convection, "eddy diffusion") do not distinguish molecular masses.

4.2) CFCs are produced in the Northern Hemisphere, so how do they get down to the Antarctic?

Vertical transport into and within the stratosphere is slow. It takes more than 5 years for a CFC molecule released at sea level to rise high enough in the stratosphere to be photolyzed. North-South transport, in both troposphere and stratosphere, is faster - there is a bottleneck in the tropics (it can take a year or two to get across the equator) but there is still plenty of time. CFC's are distributed almost uniformly as a function of latitude, with a gradient of ~10% from Northern to Southern Hemispheres. [Singh et al.]. [Elkins et al.]

4.3) Sea salt puts more chlorine into the atmosphere than CFC's.

True, but not relevant because this chlorine is in a form (HCl) that is rapidly removed from the troposphere. Even at sea level there is more chlorine present in organic compounds than in HCl, and in the upper troposphere and lower stratosphere organic chlorine dominates overwhelmingly. See section 2.1 above.

4.4) Volcanoes put more chlorine into the stratosphere than CFC's.

Short Reply: False. Volcanoes account for at most a few percent of the chlorine in the stratosphere.

Long reply: This is one of the most persistent myths in this

area. As is so often the case, there is a seed of truth at the
root of the myth. Volcanic gases are rich in Hydrogen Chloride, HCl.
As we have discussed, this gas is very soluble in water and is
removed from the troposphere on a time scale of 1-7 days, so we can
dismiss quietly simmering volcanoes as a stratospheric source, just
as we can neglect sea salt and other natural sources of HCl. (In fact
tropospheric HCl from volcanoes is neglible compared to HCl from
sea salt.) However, we cannot use this argument to dismiss MAJOR
volcanic eruptions, which can in principle inject HCl directly into
the middle stratosphere.

What is a "major" eruption? There is a sort of "Richter scale" for
volcanic eruptions, the so-called "Volcanic explosivity index" or
VEI. Like the Richter scale it is logarithmic; an eruption with a
VEI of 5 is ten times "bigger" than one with a VEI of 4. To give a
sense of magnitude, I list below the VEI for some familiar recent
and historic eruptions:

Eruption	VEI	Stratospheric Aerosol, Megatons (Mt)
Kilauea	0-1	-
Erebus, 1976-84	1-2	-
Augustine, 1976	4	0.6
St Helen's, 1980	5 (barely)	0.55
El Chichon, 1982	5	12
Pinatubo, 1991	5-6	20 - 30
Krakatau, 1883	6	50 (est.)
Tambora, 1815	7	80-200 (est.)

[Smithsonian] [Symonds et al.] [Sigurdsson] [Pinatubo] [WMO 1988]
[Bluth et al.]

Roughly speaking, an eruption with VEI>3 can penetrate the
stratosphere. An eruption with VEI>5 can send a plume up to 25km,
in the middle of the ozone layer. Such eruptions occur about once
a decade. Since the VEI is not designed specifically to measure a
volcano's impact on the stratosphere, I have also listed the total
mass of stratospheric aerosols (mostly sulfates) produced by the
eruption. (Note that St. Helens produced much less aerosol than El
Chichon - you may remember that St. Helens blew out sideways, dumping

a large ash cloud over eastern Washington, rather than ejecting its gases into the stratosphere.) Passively degassing volcanoes such as Kilauea and Erebus are far too weak to penetrate the stratosphere, but explosive eruptions like El Chichon and Pinatubo need to be considered in detail.

Before 1982, there were no direct measurements of the amount of HCl that an explosive eruption put into the stratosphere. There were, however, estimates of the total chlorine production from an eruption, based upon such geophysical techniques as analysis of glass inclusions trapped in volcanic rocks. [Cadle] [Johnston] [Sigurdsson] [Symonds et al.] There was much debate about how much of the emitted chlorine reached the stratosphere; estimates ranged from < 0.03 Mt/year [Cadle] to 0.1-1.0 Mt/year [Symonds et al.]. During the 1980's emissions of CFC's and related compounds contributed >1.2 Mt of chlorine per year to the atmosphere. [Prather et al.] This results in an annual flux of >0.3 Mt/yr of chlorine into the stratosphere. The highest estimates ofvolcanic emissions - upper limits calculated by assuming that all of the HCl from a major eruption reached and stayed in the stratosphere - were thus of the same order of magnitude as human sources. (There is NO support whatsoever for the claim - found in Dixy Lee Ray's Trashing the Planet - that a single recent eruption produced ~500 times as much chlorine as a year's worth of CFC production. This wildly inaccurate number appears to have arisen from an editorial mistake in a scientific encyclopedia.)

It is very difficult to reconcile these upper limits with the altitude and time-dependence of stratospheric HCl. The volcanic contribution to the upper stratosphere should come in sudden bursts following major eruptions, and it should initially be largest in the vicinity of the volcanic plume. Since vertical transport in the stratosphere is slow, one would expect to see the altitude profile change abruptly after a major eruption, whereas it has maintained more-or-less the same shape since it was first measured in 1975. One would also not expect a strong correlation between HCl and organochlorine compounds if volcanic injection were contributing ~50% of the total HCl. If half of the HCl has an inorganic origin, where is all that organic chlorine going?

The issue has now been largely resolved by direct measurements of

the stratospheric HCl produced by El Chichon, the most important eruption of the 1980's, and Pinatubo, the largest since 1912. It was found that El Chichon injected *0.04* Mt of HCl [Mankin and Coffey]. The much bigger eruption of Pinatubo produced less [Mankin, Coffey and Goldman], - in fact the authors were not sure that they had measured any significant increase. Analysis of ice cores leads to similar conclusions for historic eruptions [Delmas]. The ice cores show significantly enhanced levels of sulfur following major historic eruptions, but no enhancement in chlorine, showing that the chlorine produced in the eruption did not survive long enough to be transported to polar regions. It is clear, then, that even though major eruptions produce large amounts of chlorine in the form of HCl, most of that HCl either never enters the stratosphere, or is very rapidly removed from it.

Recent model calculations [Pinto et al.] [Tabazadeh and Turco] have clarified the physics involved. A volcanic plume contains approximately 1000 times as much water vapor as HCl. As the plume rises and cools the water condenses, capturing the HCl as it does so and returning it to the earth in the extensive rain showers that typically follow major eruptions. HCl can also be removed if it is adsorbed on ice or ash particles. Model calculations show that more than 99% of the HCl is removed by these processes, in good agreement with observations.

In summary:

 * Older indirect estimates of the contribution of volcanic
   eruptions to stratospheric chlorine gave results that ranged
   from much less than anthropogenic to somewhat larger than
   anthropogenic. It is difficult to reconcile the larger estimates
   with the altitude distribution of inorganic chlorine in the
   stratosphere, or its steady increase over the past 20 years.
   Nevertheless, these estimates raised an important scientific
   question that needed to be resolved by direct measurements
   in the stratosphere.

 * Direct measurements on El Chichon, the largest eruption of
   the 1980's, and on Pinatubo, the largest since 1912, show
   that the volcanic contribution is small.

 * Claims that volcanoes produce more stratospheric chlorine than
   human activity arise from the careless use of old scientific
   estimates that have since been refuted by observation.

 * Claims that a single recent eruption injected ~500 times a year's
   CFC production into the stratosphere have no scientific basis
   whatsoever.

To conclude, we need to say something about Mt. Erebus. In an
article in 21st Century (July/August 1989), Rogelio Maduro
claimed that this Antarctic volcano has been erupting constantly
for the last 100 years, emitting more than 1000 tons of chlorine
per day. This claim was repeated in Dixy Lee Ray's books.
"21st Century" is published by Lyndon LaRouche's political
associates, although LaRouche himself usually keeps a low profile
in the magazine. Mt. Erebus has in fact been simmering quietly for
over a century but the estimate of 1000 tons/day of HCl only applied
to an especially active period between 1976 and 1983. Moreover that
estimate [Kyle et al.] has been since been reduced to 167 tons/day
(0.0609 Mt/year). By late 1984 emissions had dropped by an order of
magnitude, and have remained at low levels since; HCl emissions
 at the crater rim were 19 tons/day (0.007 Mt/year) in 1986,
and 36 tons/day (0.013 Mt/year) in 1991. [Zreda-Gostynska et al.]
Since this is a passively degassing volcano (VEI=1-2 in the active
period), very little of this HCl reaches the stratosphere. The
Erebus plume never rises more than 0.5 km above the volcano,
and in fact the gas usually just oozes over the crater rim. Indeed,
one purpose of the measurements of Kyle et al. was to explain high
Cl concentrations in Antarctic snow. The only places where I have
ever seen Erebus described as a source of stratospheric chlorine is
in LaRouchian publications and in articles and books that,
incredibly, consider such documents to be reliable sources.

4.5) Space shuttles put a lot of chlorine into the stratosphere.

Simply false. In the early 1970's, when very little was known about
the role of chlorine radicals in ozone depletion, it was suggested
that HCl from solid rocket motors might have a significant effect

upon the ozone layer - if not globally, perhaps in the immediate vicinity of the launch. It was immediately shown that the effect was negligible, and this has been repeatedly demonstrated since. Each shuttle launch produces about 68 metric tons of chlorine as HCl; a full year's worth of shuttle and solid rocket launches produces about 725 tons. This is negligible compared to chlorine emissions in the form of CFC's and related compounds (1.2 million tons/yr in the 1980's, of which ~0.3 Mt reach the stratosphere each year). It is also negligible in comparison to natural sources, which produce about 75,000 tons per year. [Prather et al.] [WMO 1991].

See also the sci.space FAQ, Part 10, "Controversial Questions".

5. REFERENCES FOR PART II

A remark on references: they are neither representative nor comprehensive. There are hundreds of people working on these problems. For the most part I have limited myself to papers that are (1) widely available (if possible, Science or Nature rather than archival sources such as J. Geophys. Res.) and (2) directly related to the "frequently asked questions". (In this part, I have had to refer to archival journals more often than I would have liked, since in many cases that is the only place where the question is addressed in satisfactory detail.) Readers who want to see "who did what" should consult the review articles listed below, or, if they can get them, the extensively documented WMO reports.

Introductory Reading:

[Graedel and Crutzen] T. E. Graedel and P. J. Crutzen,
 Atmospheric Change: an Earth System Perspective, Freeman, 1993.

[Rowland 1989] F. S. Rowland, "Chlorofluorocarbons and the depletion of stratospheric ozone", Am. Sci. 77, 36, 1989.

Books and Review Articles:

[Brasseur and Solomon] G. Brasseur and S. Solomon, Aeronomy of

the Middle Atmosphere, 2nd Edition, D. Reidel, 1986.

[McElroy and Salawich] M. McElroy and R. Salawich, "Changing Composition of the Global Stratosphere", Science 243, 763, 1989.

[Rowland 1991] F. S. Rowland, "Stratospheric Ozone Depletion", Ann. Rev. Phys. Chem. 42, 731, 1991.

[Solomon] S. Solomon, "Progress towards a quantitative understanding of Antarctic ozone depletion", Nature 347, 347, 1990.

[Wallace and Hobbs] J. M. Wallace and P. V. Hobbs, Atmospheric Science: an Introductory Survey, Academic Press, 1977.

[Wayne] R. P. Wayne, Chemistry of Atmospheres, 2nd. Ed., Oxford, 1991.

[WMO 1988] World Meteorological Organization, Report of the International Ozone Trends Panel, Report # 18

[WMO 1991] World Meteorological Organization, Scientific Assessment of Ozone Depletion: 1991, Report # 25

More specialized articles:

[AASE] End of Mission Statement, second airborne arctic stratospheric expedition, NASA 30 April 1992.

[Bluth et al.] G. J. S. Bluth, C. C. Schnetzler, A. J. Krueger, and L. S. Walter, "The contribution of explosive volcanism to global atmospheric sulphur dioxide concentrations", Nature 366, 327, 1993.

[Cadle] R. Cadle, "Volcanic emissions of halides and sulfur compounds to the troposphere and stratosphere", J. Geophys. Res. 80, 1651, 1975]

[Delmas] R. J. Delmas, "Environmental Information from Ice Cores", Reviews of Geophysics 30, 1, 1992.

[Elkins et al.] J. W. Elkins, T. M. Thompson, T. H. Swanson, J. H. Butler, B. D. Hall, S. O. Cummings, D. A. Fisher, and A. G. Raffo, "Decrease in Growth Rates of Atmospheric Chlorofluorocarbons 11 and 12", Nature 364, 780, 1993.

[Eyre and Roscoe] J. Eyre and H. Roscoe, "Radiometric measurement of stratospheric HCl", Nature 266, 243, 1977.

[Fabian et al. 1979] P. Fabian, R. Borchers, K.H. Weiler, U. Schmidt, A. Volz, D.H. Erhalt, W. Seiler, and F. Mueller, "Simultaneously measured vertical profile of H2, CH4, CO, N2O, CFCl3, and CF2Cl2 in the mid-latitude stratosphere and troposphere", J. Geophys. Res. 84, 3149, 1979.

[Fabian et al. 1981] P. Fabian, R. Borchers, S.A. Penkett, and N.J.D. Prosser, "Halocarbons in the Stratosphere", Nature 294, 733, 1981.

[Farmer et al.] C.B. Farmer, O.F. Raper, and R.H. Norton, "Spectroscopic detection and vertical distribution of HCl in the troposphere and stratosphere", Geophys. Res. Lett. 3, 13, 1975.

[Harris et al.] G.W. Harris, D. Klemp, and T. Zenker, "An Upper Limit on the HCl near-surface mixing ratio over the Atlantic", J. Atmos. Chem. 15, 327, 1992.

[Johnston] D. Johnston, "Volcanic contribution of chlorine to the stratosphere: more significant to ozone than previously estimated?" Science 209, 491, 1980.

[Khalil et al.] M.A.K. Khalil, R. Rasmussen, and R. Gunawardena, "Atmospheric Methyl Bromide: Trends and Global Mass Balance" J. Geophys. Res. 98, 2887, 1993.

[Kyle et al.] P.R. Kyle, K. Meeker, and D. Finnegan, "Emission rates of sulfur dioxide, trace gases, and metals from Mount Erebus, Antarctica", Geophys. Res. Lett. 17, 2125, 1990.

[Mankin and Coffey] W. Mankin and M. Coffey, "Increased stratospheric hydrogen chloride in the El Chichon cloud",

Science 226, 170, 1983.

[Mankin, Coffey and Goldman] W. Mankin, M. Coffey and A. Goldman, "Airborne observations of SO2, HCl, and O3 in the stratospheric plume of the Pinatubo volcano in July 1991", Geophys. Res. Lett. 19, 179, 1992.

[Mano and Andreae] S. Mano and M. O. Andreae, "Emission of Methyl Bromide from Biomass Burning", Science 263, 1255, 1994.

[Penkett et al.] S.A. Penkett, R.G. Derwent, P. Fabian, R. Borchers, and U. Schmidt, "Methyl Chloride in the Stratosphere", Nature 283, 58, 1980.

[Pinatubo] Special Mt. Pinatubo issue, Geophys. Res. Lett. 19, #2, 1992.

[Pinto et al.] J. Pinto, R. Turco, and O. Toon, "Self-limiting physical and chemical effects in volcanic eruption clouds", J. Geophys. Res. 94, 11165, 1989.

[Prather et al.] M. J. Prather, M.M. Garcia, A.R. Douglass, C.H. Jackman, M.K.W. Ko, and N.D. Sze, "The Space Shuttle's impact on the stratosphere", J. Geophys. Res. 95, 18583, 1990.

[Sigurdsson] H. Sigurdsson, "Evidence of volcanic loading of the atmosphere and climate response", Palaeogeography, Palaeoclimatology, Palaeoecology 89, 277 (1989).

[Rinsland et al.] C. P. Rinsland, J. S. Levine, A. Goldman, N. D. Sze, . K. W. Ko, and D. W. Johnson, "Infrared measurements of HF and HCl total column abundances above Kitt Peak, 1977-1990: Seasonal cycles, long-term increases, and comparisons with model calculations", J. Geophys. Res. 96, 15523, 1991.

[Singh et al.] H. Singh, L. Salas, H. Shigeishi, and E. Scribner, "Atmospheric Halocarbons, hydrocarbons, and sulfur hexafluoride global distributions, sources, and sinks", Science 203, 899, 1974.

[Smithsonian] Smithsonian Report, Global Volcanism:1975-85, p 14.

[Symonds et al.] R. B. Symonds, W. I. Rose, and M. H. Reed, "Contribution of Cl and F-bearing gases to the atmosphere by volcanoes", Nature 334, 415 1988.

[Tabazadeh and Turco] A. Tabazadeh and R. P. Turco, "Stratospheric Chlorine Injection by Volcanic Eruptions: HCl Scavenging and Implications for Ozone", Science 260, 1082, 1993.

[Vierkorn-Rudolf et al.] B. Vierkorn-Rudolf. K. Bachmann, B. Schwartz, and F.X. Meixner, "Vertical Profile of Hydrogen Chloride in the Troposphere", J. Atmos. Chem. 2, 47, 1984.

[Zander et al. 1987] R. Zander, C. P. Rinsland, C. B. Farmer, and R. H. Norton, "Infrared Spectroscopic measurements of halogenated source gases in the stratosphere with the ATMOS instrument", J. Geophys. Res. 92, 9836, 1987.

[Zander et al. 1990] R. Zander, M.R. Gunson, J.C. Foster, C.P. Rinsland, and J. Namkung, "Stratospheric ClONO2, HCl, and HF concentration profiles derived from ATMOS/Spacelab 3 observations - an update", J. Geophys. Res. 95, 20519, 1990.

[Zander et al. 1992] R. Zander, M. R. Gunson, C. B. Farmer, C. P. Rinsland, F. W. Irion, and E. Mahieu, "The 1985 chlorine and fluorine inventories in the stratosphere based on ATMOS observations at 30 degrees North latitude", J. Atmos. Chem. 15, 171, 1992.

[Zreda-Gostynska et al.] G. Zreda-Gostynska, P. R. Kyle, and D. L. Finnegan, "Chlorine, Fluorine and Sulfur Emissions from Mt. Erebus, Antarctica and estimated contribution to the antarctic atmosphere", Geophys. Res. Lett. 20, 1959, 1993.

Subject: Ozone Depletion FAQ Part III: Antarctic

Archive-name: ozone-depletion/antarctic

CONTENTS

1. What is the antarctic ozone hole?

2. How big is the hole, and is it getting bigger?

3. When did the hole first appear?

4. How far back do Antarctic ozone measurements go?

5. But I heard that Dobson saw an ozone hole in 1956-58...

6. Why is the hole in the antarctic?

7. What is the evidence for the present theory?

8. Will the ozone hole keep growing?

9. Why be concerned about an ozone hole over antarctica?
    Nobody lives down there.

10. Is there an ozone hole in the arctic? if not, why not?

11. Can the hole be "plugged"?

1. What is the Antarctic ozone hole?

 For the past decade or so, ozone levels over Antarctica have fallen
to abnormally low values between late August and late November. At
the beginning of this period, ozone levels are already low, about
300 Dobson units (DU), but instead of slowly increasing as the
light comes back in the spring, they drop to 150 DU and below. In
the lower stratosphere, between 15 and 20 km, about 95% of the
ozone is destroyed. Above 25 km the decreases are small and the net
result is a thinning of the ozone layer by about 50%. In the late
spring ozone levels return to more normal values, as warm,

ozone-rich air rushes in from lower latitudes. The precise duration
varies considerably from year to year; in 1990 the hole lasted well
into December.

 In some of the popular newsmedia, as well as many books, the
term "ozone hole" is being used far too loosely. It seems that
any episode of ozone depletion, no matter how minor, now gets
called an ozone hole (e.g. 'ozone hole over Hamburg - but only for
one day'). This sloppy language trivializes the problem and blurs
the important scientific distinction between the massive ozone
losses in polar regions and the much smaller, but nonetheless
significant, ozone losses in middle latitudes. It is akin to
using "gridlock" to describe a routine traffic jam.

2. How big is the hole, and is it getting bigger?

 During the years 1978-1987 the hole grew, both in depth (total ozone
loss in a column) and in area. This growth was not monotonic but
seemed to oscillate with a two-year period (perhaps connected with
the "quasibiennial oscillation" of the stratospheric winds.) The
hole shrank dramatically in 1988 but in 1989-1991 was as large as in
1987, and in 1992-93 was larger still. In 1987 and 1989-93 it
covered the entire Antarctic continent and
part of the surrounding ocean. The exact size is determined
primarily by meteorological conditions, such as the strength of
the polar vortex in any given year. The boundary is fairly steep,
with decreases of 100-150 DU taking place in 10 degrees of
latitude, but fluctuates from day to day. On occasion, the
nominal boundary of the hole has passed over the tip of S. America,
(55 degrees S. Latitude). Australia and New Zealand are far outside
the hole, although they do experience ozone depletion, more than
is seen at comparable latitudes in the Northern hemisphere. After
the 1987 hole broke up, December ozone levels over Australia and
New Zealand were 10% below normal.
[WMO 1991] [Atkinson et al.] [Roy et al.].

3. When did the hole first appear?

 It was first observed by ground-based measurements from Halley Bay

on the Antarctic coast, during the years 1980-84. [Farman, Gardiner
and Shanklin.] At about the same time, ozone decreases were seen at
the Japanese antarctic station of Syowa; these were less dramatic than
those seen at Halley (Syowa is about 1000 km further north) and did not
receive as much attention. It has since been confirmed
by satellite measurements as well as ground-based measurements
elsewhere on the continent, on islands in the Antarctic ocean, and at
Ushaia, at the tip of Patagonia. With hindsight, one can see the hole
beginning to appear in the data around 1976, but it grew much more
rapidly in the 1980's. [Stolarski et al. 1992]

4. How far back do antarctic ozone measurements go?

 Ground-based measurements began in 1956, at Halley Bay. A few years
later these were supplemented by measurements at the South Pole and
elsewhere on the continent. Satellite measurements began in the
early 70's, but the first really comprehensive satellite data came
in 1978, with the TOMS (total ozone mapping spectrometer) and SBUV
(solar backscatter UV) instruments on Nimbus-7. The TOMS, which
finally broke down on May 7 1993, is the source for most of the
pretty pictures that one sees in review articles and the
popular press. Today there are several satellites monitoring ozone
and other atmospheric gases; the Russian Meteor-3 carries a new
TOMS, while instrument on NASA's UARS (Upper Atmosphere Research
Satellite) simultaneously measure ozone, chlorine monoxide (ClO),
and stratospheric pressure and temperature.

5. But I heard that Dobson saw an ozone hole in 1956-58...

 This is a myth, arising from a misinterpretation of an out-of-
context quotation from Dobson's paper. A glance at the original
suffices to refute it.
In his historical account [Dobson], Dobson mentioned that
when springtime ozone levels over Halley Bay were first measured,
he was surprised to find that they were about 150 DU below
corresponding levels (displaced by six months) in the Arctic.
Springtime arctic ozone levels are very high, ~450 DU; in the
Antarctic spring, however, Dobson's coworkers found ~320 DU, close
to winter levels. This was the first observation of the normal,

pre-1980 behavior of the Antarctic ozone layer: because of the tight polar vortex (see below) ozone levels remain low until late spring. In the Antarctic ozone hole, on the other hand, ozone levels decrease from these already low values. What Dobson describes is essentially the baseline from which the ozone hole is measured. [Dobson] [WMO 1989]

For those interested, here is how springtime antarctic ozone has developed from 1956 to 1991:

Halley Bay Antarctic Ozone Data

Mean October ozone column thickness, Dobson Units

From J. D. Shanklin, personal communication, 1993.
See also [Dobson], [Farman et al.], [Hamill and Toon],
[Solomon], and [WMO 1991], p. 4.6

1956	321	1975	308
1957	330	1976	283
1958	314	1977	251
1959	311	1978	284
1960	301	1979	261
1961	317	1980	227
1962	332	1981	237
1963	309	1982	234
1964	318	1983	210
1965	281	1984	201
1966	316	1985	196
1967	323	1986	248
1968	301	1987	163
1969	282	1988	232
1970	282	1989	164
1971	299	1990	179
1972	304	1991	155
1973	289	1992	142
1974	274	1993	117

6. Why is the hole in the Antarctic?

This was a mystery when the hole was first observed, but
it is now well understood. I shall limit myself to a
brief survey of the present theory, and refer the reader to two
excellent nontechnical articles [Toon and Turco] [Hamill and Toon]
for a more comprehensive discussion. Briefly, the unusual
physics and chemistry of the Antarctic stratosphere allows the
inactive chlorine "reservoir" compounds to be converted into ozone-
destroying chlorine radicals. While there is no more chlorine over
antarctica than anywhere else, in the antarctic spring most of
the chlorine is in a form that can destroy ozone.

The story takes place in six acts, some of them occurring
simultaneously on parallel stages:

i. The Polar Vortex

As the air in the antarctic stratosphere cools and descends during
the winter, the Coriolis effect sets up a strong westerly
circulation around the pole. When the sun returns in the spring the
winds weaken, but the vortex remains stable until November. The air
over antarctica is largely isolated from the rest of the
atmosphere, forming a gigantic reaction vessel. The vortex is not
circular, it has an oblong shape with the long axis extending out
over Patagonia.

(For further information about the dynamics of the polar vortex see
[Schoeberl and Hartmann], [Tuck 1989], [AASE], [Randel], [Plumb],
and [Waugh]). There is currently some controversy over just how isolated
the air in the vortex is. According to Tuck, the vortex is better
thought of as a flow reactor than as a containment vessel; ozone-rich
air enters the vortex from above while ozone-poor and ClO-rich air is
stripped off the sides. Recent tracer measurements lend some support
to this view, but the issue is unresolved. See [Randel] and [Plumb].)
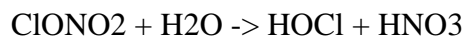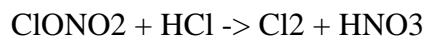
ii. Polar Stratospheric Clouds ("PSC")

The Polar vortex is extremely cold; temperatures in the lower
stratosphere drop below -80 C. Under these conditions large numbers
of clouds appear in the stratosphere. These clouds are composed

largely of nitric acid and water, probably in the form of crystals of nitric acid trihydrate ("NAT"), $HNO_3.3(H_2O)$. Stratospheric clouds also form from ordinary water ice (so-called "Type II PSC"), but these are much less common; the stratosphere is very dry and water-ice clouds only form at the lowest temperatures.

iii. Reactions Catalyzed by Stratospheric Clouds

Most of the chlorine in the stratosphere ends up in one of the reservoir compounds, Chlorine Nitrate ($ClONO_2$) or Hydrogen Chloride (HCl). Laboratory experiments have shown, however, that these compounds, ordinarily inert in the stratosphere, do react on the surfaces of polar stratospheric cloud particles. HCl dissolves into the particles as they grow, and when a $ClONO_2$ molecule becomes adsorbed the following reactions take place:

$ClONO_2 + HCl \rightarrow Cl_2 + HNO_3$

$ClONO_2 + H_2O \rightarrow HOCl + HNO_3$

The Nitric acid, HNO_3, stays in the cloud particle.

In addition, stratospheric clouds catalyze the removal of Nitrogen Oxides ("NOx"), through the reactions:

$N_2O_5 + H_2O \rightarrow 2\ HNO_3$

$N_2O_5 + HCl \rightarrow ClNO_2 + HNO_3$
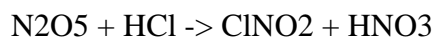
Since N_2O_5 is in (gas-phase) equilibrium with NO_2:

$2\ N_2O_5 \leftrightarrow 4\ NO_2 + O_2$
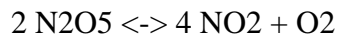
this has the effect of removing NO_2 from the gas phase and sequestering it in the clouds in the form of nitric acid, a process called "denoxification" (removal of "NOx").

iv. Sedimentation and Denitrification

The clouds may eventually grow big enough so that they settle out of the stratosphere, carrying the nitric acid with them

("denitrification"). Denitrification enhances denoxification.
If, on the other hand, the cloud decomposes while in the
stratosphere, nitrogen oxides are returned to the gas phase.
Presumably this should be called "renoxification", but
I have not heard anyone use this term :-).
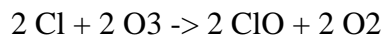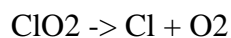
v. Photolysis of active chlorine compounds

 The Cl2 and HOCl produced by the heterogeneous reactions are
easily photolyzed, even in the antarctic winter when there is
little UV present. The sun is always very low in the polar winter,
so the light takes a long path through the atmosphere and the
short-wave UV is selectively absorbed. Molecular chlorine,
however, absorbs visible and near-UV light:

    Cl2 + hv -> 2 Cl

    Cl + O3 -> ClO + O2
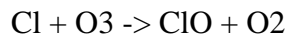
The effect is to produce large amounts of ClO. This ClO would
ordinarily be captured by NO2 and returned to the ClONO2 reservoir,
but "denoxification" and "denitrification" prevent this by removing
NO2.

vi. The chlorine peroxide mechanism

 As discussed in Part I, Cl and ClO can form a catalytic cycle that
efficiently destroys ozone. This cycle uses free oxygen atoms,
however, which are only abundant in the upper stratosphere, whereas
the ozone hole forms in the lower stratosphere. Instead, the
principal mechanism involves chlorine peroxide, ClOOCl (often
referred to as the "ClO dimer"):

    ClO + ClO -> ClOOCl
    ClOOCl + hv -> Cl + ClO2
    ClO2 -> Cl + O2
    2 Cl + 2 O3 -> 2 ClO + 2 O2

    Net: 2 O3 -> 3 O2
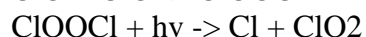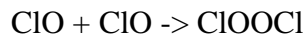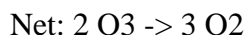
 At polar stratospheric temperatures this sequence is extremely fast

and it dominates the ozone-destruction process. The second step, photolysis of chlorine peroxide, requires UV light which only becomes abundant in the lower stratosphere in the spring. Thus one has a long buildup of ClO and ClOOCl during the winter, followed by massive ozone destruction in the spring. This mechanism is believed to be responsible for about 70% of the antarctic ozone loss.

Another mechanism that has been identified involves chlorine and bromine:

```
   ClO + BrO -> Br + Cl + O2
   Br + O3 -> BrO + O2
   Cl + O3 -> ClO + O2
   ----------------------
   Net: 2 O3 -> 3 O2
```

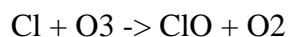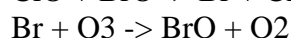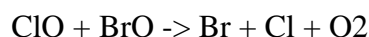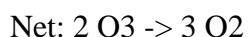 This is believed to be responsible for ~25% of the antarctic ozone depletion. Additional mechanisms have been suggested, but they seem to be less important. [WMO 1991]

(For further information on the "perturbed chemistry" of the antarctic stratosphere, see [Solomon], [McElroy and Salawich], and [WMO 1989, 1991]).

7. What is the evidence for the present theory?

The evidence is overwhelming - the results from a single 1987 expedition (albeit a crucial one) fill two entire issues of the Journal of Geophysical Research. What follows is a very sketchy summary; for more information the reader is directed to [Solomon] and to [Anderson et al.].

 The theory described above (which is often called the "PSC theory") was developed during the years 1985-87. At the same time, others proposed completely different mechanisms, making no use of chlorine chemistry. The two most prominent alternative explanations were one that postulated large increases in nitrogen oxides arising from enhanced solar activity, and one that postulated an upwelling of ozone-poor air from the troposphere into the cold stratospheric vortex. Each hypothesis made definite

predictions, and a program of measurements was carried out to test these. The solar activity hypothesis predicted enhanced NOx, whereas the measurements show unusually low NOx ("denoxification), in accordance with the PSC hypothesis. The "upwelling" hypothesis predicted upward air motion in the lower stratosphere, which is inconsistent with measurements of atmospheric tracers such as N2O which show that the motion is primarily downwards.

Positive evidence for the PSC theory comes from ground-based and airborne observations of the various chlorine-containing compounds. These show that the reservoir species HCl and ClONO2 are extensively depleted in the antarctic winter and spring, while the concentration of the active, ozone-depleting species ClO is strongly enhanced. Measurements also show enormously enhanced concentrations of the molecule OClO. This is formed by a side-reaction in the BrO/ClO mechanism described above.

Further evidence comes from laboratory studies. The gas-phase reactions have been reproduced in the laboratory, and shown to proceed at the rates required in order for them to be important in the polar stratosphere. [Molina et al. 1990] [Sander et al.] [Trolier et al.] [Anderson et al.]. The production of active chlorine from reservoir chlorine on ice and sulfuric acid surfaces has also been demonstrated in the laboratory [Tolbert et al. 1987,1988] [Molina et al. 1987]. (Recently evidence for these reactions has been found in the arctic stratosphere as well: air parcels that had passed through regions where the temperature was low enough to form PSC's were found to have anomalously low concentrations of HCl and anomalously high concentrations of ClO [AASE].)

The "smoking gun", however, is usually considered to be the simultaneous in-situ measurements of a variety of trace gases from an ER-2 stratospheric aircraft (a converted U2 spy plane) in August-October 1987. [Tuck et al.] These measurements demonstrated a striking "anticorrelation" between local ozone concentrations and ClO concentrations. Upon entering the "hole", ClO concentrations suddenly jump by a factor of 20 or more, while ozone concentrations drop by more than 50%. Even the local fluctuations in the concentrations of the two species are anticorrelated. [Anderson et al.]

In summary, the PSC theory explains the following observations:

1. The ozone hole occupies the region of the polar vortex where
   temperatures are below -80 C and where polar stratospheric clouds
   are abundant.

2. The ozone hole is confined to the lower stratosphere.

3. The ozone hole appears when sunlight illuminates the vortex, and
   disappears soon after temperatures rise past -80 C, destroying PSC's.

4. The hole is associated with extremely low concentrations of NOx.

5. The hole is associated with very low concentrations of the chlorine
   "reservoirs", HCl and ClONO2, and very high concentrations of active
   chlorine compounds, ClO, and byproducts such as OClO.

6. Inside the hole, the concentrations of ClO and ozone are precisely
   anticorrelated, high ClO being accompanied by low ozone.

7. Laboratory experiments demonstrate that chlorine reservoir compounds
   do react to give active chlorine on the surfaces of ice particles.

8. Airborne measurements in the arctic stratosphere show that air
   which has passed through regions containing PSC's is low in
   reservoir chlorine and high in active chlorine.

The antarctic ozone hole, once a complete mystery, is now
one of the best understood aspects of the entire subject; it is
much better understood than the small but steadily growing ozone
depletion at mid latitudes, for example.

8. Will the ozone hole keep growing?

 To answer this, we need to consider separately the lateral
dimensions (the "area" of the hole), the vertical dimension (its
"depth") and the temporal dimension (how long the hole lasts.)

a.) Lateral Extent

Let us define the "hole" to be the
region where the total ozone column is less than 200 DU,
i.e. where total ozone has fallen to less than 2/3 of normal
springtime antarctic values. Defined thus, the hole is always
confined to the south polar vortex, south of ~55 degrees. At
present it does not fill the whole vortex, only the central core
where stratospheric temperatures are less than ~-80 C. Typically
this region is south of ~65 degrees, although there is a great deal
of variation - in some years the center of the vortex is displaced
well away from the pole, and the nominal boundary of the hole has
on a few occasions passed over the tip of Chile. As stratospheric
chlorine continues to rise, the hole might "fill out" the vortex;
this could as much as double its area. [Schoeberl and Hartmann]. So
far this does not seem to be happening. The 1992 hole was 15-25%
larger than previous years, and the 1993 hole appears to be almost
as large. This increase is probably due to the
stratospheric sulfate aerosols from the July 1991 eruption of Mt.
Pinatubo, which behave in some respects like polar stratospheric
clouds. [Solomon et al. 1993] These aerosols settle out of the
stratosphere after 2-3 years, so the increases seen in 1992 are
expected to be temporary. In any case, it cannot grow beyond
~55 degrees without a major change in the antarctic wind patterns
that would allow the vortex to grow. Such a change could
conceivably accompany global warming: the greenhouse effect warms
the earth's surface, but cools the stratosphere. There is no
reason to expect the hole to expand out over Australia, S. Africa,
etc., although these regions could experience further ozone
depletion after the hole breaks up and the ozone-poor air drifts
north.

b. Vertical Depth

 The hole is confined to the lower stratosphere, where the
clouds are abundant. In this region the ozone is essentially
gone. The upper stratosphere is much less affected, however, so
that overall column depletion comes to ~50%. As stratospheric
chlorine concentrations continue to increase over the next 10
years or so, some penetration to higher altitudes may take place,
but large increases in depth are not expected. (Once again,
aerosols from Mt. Pinatubo have allowed the 1992 and 1993 holes
to extend over a larger altitude range than usual, both higher

and lower, but this is probably a temporary effect.)

c. Duration of the hole

Here we might see major effects. The hole is destroyed in late spring/early summer when the vortex breaks up and warm, ozone-rich air rushes in. If the stratosphere cools, the vortex becomes more stable and lasts longer. As mentioned above, the greenhouse effect actually cools the stratosphere. There is a more direct cooling mechanism, however - remember that the absorption of solar UV by ozone is the major source of heat in the stratosphere, and is the reason that the temperature of the stratosphere increases with altitude. Depletion of the ozone layer therefore cools the stratosphere, and in this sense the hole is self-stabilizing. In future years we might see more long-lived holes like that in 1990, which survived into early December.

(The relationship between ozone depletion and climate change is complicated, and best dealt with in a separate FAQ, preferably written by someone other than myself :-))

9. Why be concerned about an ozone hole over antarctica?
   Nobody lives down there.

First of all, even though the ozone hole is confined to the antarctic, its effects are not. After the hole breaks up in the spring, ozone-poor air drifts north and mixes with the air there, resulting in a transient decrease at middle and high latitudes. This has been seen as far north as Australia [WMO 1991][Roy et al.] [Atkinson et al.] On a time scale of months short-wave UV regenerates the ozone, but it is believed that this "dilution" may be a major cause of the much smaller global ozone depletion, ~3% per decade, that has been observed. Moreover, the air from the ozone hole is also rich in ClO and can destroy more ozone as it mixes with ozone-rich air. Even during the spring, the air in the vortex is not completely isolated, although there is some controversy over the extent to which the ozone hole acts as a "chemical processor" for the earth's atmosphere.
([Tuck 1989] [Schoeberl and Hartmann] [AASE] [Randel] [Waugh].)

 From a broader standpoint, the ozone hole is a distant early
warning message. Because of its unusual meteorological properties
the antarctic stratosphere is especially sensitive to chemical
perturbations; the natural mechanisms by which chlorine is
sequestered in reservoirs fail when total stratospheric chlorine
reaches about 2 parts per billion. This suggests that allowing
CFC emissions to increase by 3% per year, as was occurring during
the 1980's, is unwise, to say the least. The emission reduction
schedules negotiated under the Montreal Protocol (as revised in
1990 and 1992) lead to a projected maximum of ~4 ppb total strat.
chlorine in the first decade of the 21st century, followed by a
gradual decrease. Letting emissions increase at 3%/year would have
led to >16 ppb total stratospheric chlorine by 2040, and even a
freeze at 1980 rates would have led to >10 ppb. [Prather et al.].

10. Is there an ozone hole in the arctic? if not, why not?

 There is no massive ozone loss in the arctic, although there is
unusually large springtime ozone depletion, so the word "hole" is
not appropriate. I like the expression "arctic ozone dimple" but
this is not canonical :-). The arctic polar vortex is much weaker
than the antarctic, arctic temperatures are several degrees higher,
and polar stratospheric clouds are much less common (and they tend
to break up earlier in the spring.) Thus even though wintertime ClO
gets very high, as high as antarctic ClO in 1991-2, it does not
remain high through the spring, when it counts. [AASE] (Recent UARS
measurements, however, indicate that in 1993 arctic stratosphere
temperatures stayed low enough to retain PSC's until late February,
and ClO remained high into March. Large ozone depletions, ~10-20%,
have now (spring 1993) been reported for high latitudes in the
Northern Hemisphere; these still do not qualify as an "ozone hole"
but they do seem to indicate that the same physics and chemistry
are operating, albeit with much less efficiency. [Waters et al.]
[Gleason et al.])

 If "global warming" does indeed take place during the first
few decades of the next century, we may see a dramatic change in
arctic ozone. The greenhouse effect warms the surface of the
earth, but at the same time cools the stratosphere. Since there
is much less air in the stratosphere, 2-3 degrees of surface

warming corresponds to a much larger decrease in stratospheric temperatures, as much as 10 degrees. This could lead to a true ozone hole in the arctic, although it would still probably be smaller and weaker than the antarctic hole. [Austin et al.]

The 27 August issue of Science magazine contains 8 papers devoted to arctic ozone depletion in the winter of 1991-92. [AASE]

11. Can the hole be "plugged"?

The present ozone hole, while serious, is not in itself catastrophic. UV radiation is always low in polar regions since the sun takes a long path through the atmosphere and hence through the ozone layer. There may be serious consequences for marine life in the antarctic ocean, which is adapted to the normally low UV levels. When the hole breaks up in summer, there may be temporary increases in UV-b at high latitudes of the southern hemisphere as air that is poor in ozone and rich in "active", ozone-destroying forms of chlorine mixes with the air outside.

 Nevertheless it looks like we are stuck with the hole for the next 50 years at least, and we don't know what new surprises the atmosphere has in store for us. Thus, some atmospheric scientists have been exploring the possibility of "fixing" the hole by technological means. All such schemes proposed so far are highly controversial, and there are no plans to carry any of them out until the chemistry and dynamics of the stratosphere are much better understood than they are at present.

 It should be made clear at the beginning that there is no point in trying to replace the ozone directly. The amounts are far too large to be transported to the stratosphere, and the antarctic mechanisms are so fiendishly efficient that they will easily destroy added ozone (recall that where the catalytic cycles operate, ~95% of the ozone is gone, in spite of the fact that the sun is generating it all the time.) It is far better to try to remove the halogen catalysts. One suggestion made a few years ago was to release sodium metal into the stratosphere, in hopes that it would form sodium chloride crystals which would settle out. The problem is that the microcrystals remain suspended as long as they

are small, and can play the same role as clouds and aerosols in converting reservoir chlorine to active chlorine.

A second suggestion is to destroy the CFC's while they are still in the troposphere, by photolyzing them with high-powered infrared lasers installed on mountainsides. (CFC's and similar molecules can absorb as many as 30 infrared photons from a single laser pulse, a phenomonon known as infrared multiphoton dissociation). The chlorine atoms released would quickly be converted to HCl and rained out. The power requirements of such a project are daunting, however, and it appears that much of the laser radiation would be shifted out of the desired frequency range by stimulated raman scattering. [Stix]

A more serious possibility is being explored by one of the discoverers of chlorine-catalyzed ozone depletion, Ralph Cicerone, together with Scott Elliot and Richard Turco [Cicerone et al. 1991,1992]. They considered the effects of dumping ~50,000 tons of ethane or propane, several hundred planeloads, into the antarctic stratosphere every spring. The hydrocarbons would react rapidly with the Cl-containing radicals to give back the reservoir HCl. The hydrocarbons themselves are fairly reactive and would decompose by the end of a year, so the treatment would have to be repeated annually. The chlorine would not actually be removed from the stratosphere, but it would be bound up in an inert form - in other words, the catalyst would be "poisoned". There are no plans to carry this or any other scheme out in the near future; to quote from Cicerone et al. (1991), "Before any actual injection experiment is undertaken there are many scientific, technical, legal and ethical questions to be faced, not the least of which is the issue of unintended side effects."

REFERENCES FOR PART III

A remark on references: they are neither representative nor comprehensive. There are hundreds of people working on these problems. For the most part I have limited myself to papers that are (1) widely available (if possible, Science or Nature rather than archival sources such as J. Geophys. Res.) and (2) directly related to the "frequently asked questions". This gives very short

shrift to much important work; for example, I say very little about
stratospheric NOx, even though a detailed accounting of chemistry
and transport of the nitrogen oxides is one of the major goals
of current research. Readers who want to see "who did what" should
consult the review articles listed below, or, if they can get them,
the extensively documented WMO reports.

Introductory Reading:

[Graedel and Crutzen] T. Graedel and P. Crutzen, Atmospheric
 Change: an Earth System Perspective, Freeman, 1993.

[Hamill and Toon] P. Hamill and O. Toon, "Polar stratospheric
clouds and the ozone hole", Physics Today December 1991.

[Stolarski] Richard Stolarski, "The Antarctic Ozone Hole", Sci.
American 1 Jan. 1988. (this article is now seriously out of date,
but it is still a good place to start).

[Toon and Turco] O. Toon and R. Turco, "Polar Stratospheric Clouds
and Ozone Depletion", Sci. Am. June 1991

[Zurer] P. S. Zurer, "Ozone Depletion's Recurring Surprises
Challenge Atmospheric Scientists", Chemical and Engineering News,
24 May 1993, pp. 9-18.

Books and Review Articles:

[Anderson, Toohey and Brune] J.G. Anderson, D. W. Toohey, and W. H.
Brune, "Free Radicals within the Antarctic vortex: the role of
CFC's in Antarctic Ozone Loss", Science 251, 39 (4 Jan. 1991).

[McElroy and Salawich] M. McElroy and R. Salawich, "Changing
Composition of the Global Stratosphere", Science 243, 763, 1989.

[Solomon] S. Solomon, "Progress towards a quantitative
understanding of Antarctic ozone depletion",
Nature 347, 347, 1990.

[Wayne] R. P. Wayne, Chemistry of Atmospheres, 2nd. Ed.,
Oxford, 1991, Ch. 4.

[WMO 1989] World Meteorological Organization Global Ozone Research
and Monitoring Project - Report #20, "Scientific Assessment of
Stratospheric Ozone: 1989".

[WMO 1991] World Meteorological Organization Global Ozone Research
and Monitoring Project - Report #25, "Scientific Assessment of
Ozone Depletion: 1991".

More Specialized:

[AASE] Papers resulting from the Second Airborne Arctic Stratosphere
 Expedition, published in Science 261, 1128-1157, 27 Aug. 1993.

[Atkinson et al.] R. J. Atkinson, W. A. Matthews, P. A. Newman,
 and R. A. Plumb, "Evidence of the mid-latitude impact of Antarctic
 ozone depletion", Nature 340, 290, 1989.

[Austin et al.] J. Austin, N. Butchart, and K. P. Shine,
"Possibility of an Arctic ozone hole in a doubled-CO2 climate",
Nature 360, 221, 1992.

[Cicerone et al. 1991] R. Cicerone, S. Elliot, and R. Turco,
"Reduced Antarctic Ozone Depletions in a Model with Hydrocarbon
Injections", Science 254, 1191, 1991.

[Cicerone et al. 1992] R. Cicerone, S. Elliot, and R. Turco,
"Global Environmental Engineering", Nature 356, 472, 1992.

[Dobson] G. M. B. Dobson, "Forty Years' research on atmospheric
ozone at Oxford", Applied Optics, 7, 387, 1968.

[Farman et al.] J. C. Farman, B. G. Gardiner, and J. D. Shanklin,
"Large losses of total ozone in Antarctica reveal seasonal ClOx/NOx
interaction", Nature 315, 207, 1985.

[Frederick and Alberts] J. Frederick and A. Alberts, "Prolonged
 enhancement in surface ultraviolet radiation during the Antarctic

spring of 1990", Geophys. Res. Lett. 18, 1869, 1991.

[Gleason et al.] J. Gleason, P. Bhatia, J. Herman, R. McPeters, P. Newman, R. Stolarski, L. Flynn, G. Labow, D. Larko, C. Seftor, C. Wellemeyer, W. Komhyr, A. Miller, and W. Planet, "Record Low Global Ozone in 1992", Science 260, 523, 1993.

[Molina et al. 1987] M. J. Molina, T.-L. Tso, L. T. Molina, and F.C.-Y. Yang, "Antarctic stratospheric chemistry of chlorine nitrate, hydrogen chloride, and ice: Release of active chlorine", Science 238, 1253, 1987.

[Molina et al. 1990] M. Molina, A. Colussi, L. Molina, R. Schindler, and T.-L. Tso, "Quantum yield of chlorine atom formation in the photodissociation of chlorine peroxide (ClOOCl) at 308 nm", Chem. Phys. Lett. 173, 310, 1990.

[Plumb] A. Plumb, "Mixing and Matching", Nature 365, 489-90, 1993. (News and Views)

[Prather et al.] M.J. Prather, M.B. McElroy, and S.C. Wofsy, "Reductions in ozone at high concentrations of stratospheric halogens", Nature 312, 227, 1984.

[Randel] W. Randel, "Ideas flow on Antarctic vortex", Nature 364, 105, 1993 (News and Views)

[Roy et al.] C. Roy, H. Gies, and G. Elliott, "Ozone Depletion", Nature 347, 235, 1990. (Scientific Correspondence)

[Sander et al.] S.P. Sander, R.J. Friedl, and Y.K. Yung, "Role of the ClO dimer in polar stratospheric chemistry: rate of formation and implications for ozone loss", Science 245, 1095, 1989.

[Schoeberl and Hartmann] M. Schoeberl and D. Hartmann, "The dynamics of the stratospheric polar vortex and its relation to springtime ozone depletions", Science 251, 46, 1991.

[Solomon et al. 1993] S. Solomon, R. Sanders, R. Garcia, and J. Keys, "Increased chlorine dioxide over Antarctica caused by volcanic aerosols from Mt. Pinatubo", Nature 363, 245, 1993.

[Stix] T. H. Stix, "Removal of Chlorofluorocarbons from the earth's atmosphere", J. Appl. Physics 60, 5622, 1989.

[Stolarski et al. 1992] R. Stolarski, R. Bojkov, L. Bishop, C. Zerefos, J. Staehelin, and J. Zawodny, "Measured Trends in Stratospheric Ozone", Science 256, 342 (17 April 1992)

[Tolbert et al. 1987] M.A. Tolbert, M.J. Rossi, R. Malhotra, and D.M. Golden, "Reaction of chlorine nitrate with hydrogen chloride and water at Antarctic stratospheric temperatures", Science 238, 1258, 1987.

[Tolbert et al. 1988] M.A. Tolbert, M.J. Rossi, and D.M. Golden, "Antarctic ozone depletion chemistry: reactions of N2O5 with H2O and HCl on ice surfaces", Science 240, 1018, 1988.

[Trolier et al.] M. Trolier, R.L. Mauldin III, and A. Ravishankara, "Rate coefficient for the termolecular channel of the self-reaction of ClO", J. Phys. Chem. 94, 4896, 1990.

[Tuck 1989] A. F. Tuck, "Synoptic and Chemical Evolution of the Antarctic Vortex in late winter and early spring, 1987: An ozone processor", J. Geophys. Res. 94, 11687, 1989.

[Tuck et al.] A. F. Tuck, R. T. Watson, E. P. Condon, and J. J. Margitan, "The planning and execution of ER-2 and DC-8 aircraft flights over Antarctica, August and September, 1987" J. Geophys. Res. 94, 11182, 1989.

[Waters et al.] J. Waters, L. Froidevaux, W. Read, G. Manney, L. Elson, D. Flower, R. Jarnot, and R. Harwood, "Stratospheric ClO and ozone from the Microwave Limb Sounder on the Upper Atmosphere Research Satellite", Nature 362, 597, 1993.

[Waugh] D. W. Waugh, "Subtropical stratospheric mixing linked to disturbances in the polar vortices", Nature 365, 535, 1993.

Subject: Ozone Depletion FAQ Part IV: UV Radiation and its Effects

CONTENTS

1. What is "UV-B"?

 "UV-B" refers to UV light having a wavelength between 280 and 320 nm. These wavelengths are on the lower edge of ozone's UV absorption band, in the so-called "Huggins bands". They are absorbed by ozone, but less efficiently than shorter wavelengths ("UV-C"). (The absorption cross-section of ozone increases by more than 2 orders of magnitude between 320 nm and the peak value at ~250 nm.) Depletion of the ozone layer would first of all result in increased UV-B. In principle UV-C would also increase, but it is absorbed so efficiently that a very large depletion would have to take place in order for significant amounts to reach the earth's surface. UV-B and UV-C are absorbed by DNA and other biological macromolecules, inducing photochemical reactions. UV radiation with

a wavelength longer than 320 nm is called "UV-A". It is not
absorbed by ozone, but it is not believed to be especially
dangerous. (See, however, question #6.)

2. How does UV-B vary from place to place?

A great deal. It is strongest at low latitudes and high altitudes.
At higher latitudes, the sun is always low in the sky so that it takes
a longer path through the atmosphere and more of the UV-B is absorbed.
For this reason, ozone depletion is likely to have a greater impact on
local ecosystems, such as terrestrial plants and the Antarctic marine
phytoplankton, than on humans or their livestock.
UV also varies with altitude and local cloud cover. These trends can
be seen in the following list of annually-averaged UV indices for
several US cities [Roach] (units are arbitrary - I don't know
precisely how this index is defined though I assume it is
proportional to some integral over the UV-b region of the spectrum)

     Minneapolis, Minnesota   570
     Chicago, Illinois   637
     Washington, DC   683
     San Francisco, California   715
     Los Angeles, California   824
     Denver, Colorado   951
     Miami, Florida   1028
     Honolulu, Hawaii   1147

It should be noted that skin cancer rates show a similar trend.
(See below).

3. Is UV-B at the earth's surface increasing?

Yes, in some places; no, in others.

Very large increases - up to a factor of 2 - have been seen even
in the outer portions of the Antarctic hole. [Frederick and
Alberts]

Small increases, of order 1% per year, have been measured in the
Swiss Alps. [Blumthaler and Ambach] These net increases are small
compared to natural day-to-day fluctuations, but they are actually
a little larger than would be expected from the amount of ozone
depletion over the same period.

In urban areas of the US, UV-B
levels showed no significant increase (and in most cases actually
decreased a little) between 1974 and 1985. [Scotto et al.]. This
is probably due to increasing urban pollution, including low-level
ozone and aerosols. [Grant] Tropospheric ozone is actually
somewhat more effective at absorbing UV than stratospheric ozone,
because UV light is scattered much more in the troposphere, and
hence takes a longer path. [Bruehl and Crutzen] Increasing
amounts of tropospheric aerosols, from urban and industrial
pollution, may also offset UV-B increases at the ground. [Liu et
al.] [Madronich 1992, 1993] [Grant] There have been questions about
the suitability of the instruments used by Scotto et al.; they were
not designed for measuring long-term trends, and they put too much
weight on regions of the UV spectrum which are not appreciably
absorbed by ozone in any case. [WMO 1989] Nevertheless it seems
clear that so far ozone depletion over US cities is small enough to
be largely offset by competing factors. Tropospheric ozone and aerosols
have increased in rural areas of the US and Europe as well, so
these areas may also be screened from the effects of ozone depletion.

A recent study [Kerr and McElroy] has found convincing evidence of
UV-B increases in Toronto, Canada over the period 1989-1993. The UV
intensity at 300 nm increased by 35% per year in winter and 7% per
year in summer. At this wavelength 99% of the total UV is absorbed,
so these represent large increases in a small number, and do not
represent a health hazard; nevertheless these wavelengths play a
disproportionately large role in skin carcinoma and plant damage
since DNA absorbs strongly there. Total UV-B irradiance, weighted
in such a way as to correlate with incidence of sunburn ("erythemally
active radiation"), increased by 5% per year in winter and 2% per year
in summer. The trends are strongly influenced by the unusually large,
and probably transient, ozone losses in these regions in the years
1992-1993 (see part I) and should therefore not be extrapolated into
the future; they do provide strong evidence of a link between ozone
loss at middle latitudes and total UV-B radiation.

Indirect evidence for increases has been obtained in the Southern Hemisphere, where stratospheric ozone depletion is larger and tropospheric ozone (and aerosol pollution) is lower. Biologically weighted UV-B irradiances at a station in New Zealand were 1.4-1.8 times higher than irradiances at a comparable latitude and season in Germany, of which a factor of 1.3-1.6 can be attributed to differences in the ozone column over the two locations [Seckmeyer and McKenzie]. In the southern hemisphere summer, the noontime UV-B irradiance at Ushaia in Tierra del Fuego is 45% above what would be predicted were there no ozone depletion. [Frederick et al. 1993]

In comparing UV-B estimates, one must pay careful attention to exactly what is being reported. One wants to know not just whether there is an increase, but how much increase there is at any given wavelength, since the shorter wavelengths are more dangerous. Different measuring instruments have different spectral responses, and are more or less sensitive to various spectral regions. [Wayne, Rowland 1991]. Wavelength-resolving instruments, such as the spectroradiometers being used in Antarctica, Argentina, and Toronto, are the most informative, as they allow one to distinguish the effects of ozone trends from those due to clouds and aerosols. [Madronich 1993] [Kerr and McElroy].

4. What is the relationship between UV radiation and skin cancer?

There are three kinds of skin cancer, basal cell carcinomas, squamous cell carcinomas, and melanomas. In the US there were 500,000 cases of the first, 100,000 of the second, and 27,600 of the third in 1990. [Wayne] More than 90% of the skin carcinomas in the US are attributed to UV-b exposure: their frequency varies sharply with latitude, just as UV does. The mechanism by which UV-B induces carcinomas has been identified - the pyrimidine bases in the DNA molecule form dimers when stimulated by UV-B radiation. [Tevini]. Fortunately, these cancers are relatively easy to treat if detected in time, and are rarely fatal. Skin carcinoma rates vary sharply with latitude, just as UV-B does. Fair-skinned people of North European ancestry are particularly susceptible. The highest rates in the world are found in Queensland, a northerly province of Australia.

[Madronich and deGruiji] have estimated the expected increases in
skin carcinoma rates due to ozone depletion over the period 1979-1992:

Lat.	% ozone loss 1979-1992	% increase in rate, basal cell carcinoma	% increase in rate, squamous cell carcinoma
55N	7.4 +-1.3	13.5 +-5.3	25.4 +-10.3
35N	4.8 +-1.4	8.6 +-4.0	16.0 +-7.6
15N	1.5 +-1.1	2.7 +-2.4	4.8 +-4.4
15S	1.9 +-1.3	3.6 +-2.6	6.5 +-4.8
35S	4.0 +-1.6	8.1 +-3.6	14.9 +-6.8
55S	9.0 +-1.5	20.4 +-7.4	39.3 +-15.1

Of course, the rates themselves are much smaller at high latitudes,
where the relative increases in rates are large. These estimates do
not take changes in lifestyle into consideration.

Malignant melanoma is much more dangerous, but its connection
with UV exposure is not well understood. There seems to a correlation
between melanomas and brief, intense exposures to UV (long before
the cancer appears.) Melanoma incidence is definitely correlated with
latitude, with twice as many deaths (relative to state population)
in Florida or Texas as in Wisconsin or Montana, but this correlation
need not imply a causal relationship. Some claim that UV-A, which is
not absorbed by ozone, is involved. [Skolnick] [Setlow et al.]

5. Is ozone loss to blame for the melanoma upsurge?

A few physicians have said so, but most others think not.
[Skolnick]

First of all, UV-B has not, so far, increased very much, at least
in the US and Europe.

Second, melanoma takes 10-20 years to develop. There hasn't been
enough time for ozone depletion to play a significant role.

Third, the melanoma epidemic has been going on since the 1940's.

Recent increases in rates may just reflect better reporting, or
the popularity of suntans in the '60's and '70's. (This becomes
more likely if UV-A is in fact involved.)

6. Does UV-B cause cataracts?

While the evidence for this is indirect, it is very plausible.

The lens of the eye is a good UV-filter, protecting the delicate
structures in the retina. Too much UV results in short-term "snow
blindness", but the effects of prolonged, repeated exposure are
not known. People living in naturally high UV environments such
as Bolivia or Tibet do have a high incidence of cataracts, and overall
cataracts are more frequently seen at lower latitudes. [Tevini]

7. Are sheep going blind in Chile?

If they are, it's not because of ozone depletion.

For a short period each year, the edge of the ozone hole passes
over Tierra del Fuego, at the southern end of the South American
continent. This has led to a flurry of reports of medical damage
to humans and livestock. Dermatologists claim that they are seeing
more patients with sun-related conditions, nursery owners report
damage to plants, a sailor says that his yacht's dacron sails have
become brittle, and a rancher declares that 50 of his sheep,
grazing at high altitudes, suffer "temporary cataracts" in the
spring. (Newsweek, 9 December 1991, p. 43; NY Times, 27 July
1991, p. C4; 27 March 1992, p. A7).

These claims are hard to believe. At such a high latitude,
springtime UV-B is naturally very low and the temporary increase
due to ozone depletion still results in a UV fluence that is well
below that found at lower latitudes. Moreover, the climate of
Patagonia is notoriously cold and wet. (There is actually more of
a problem in the summer, after the hole breaks up and ozone-poor
air drifts north. The ozone depletion is smaller, but the
background UV intensity is much higher.) There may well be effects
on local species, adapted to low UV levels, but even these are

not expected to appear so soon. It was only in 1987 that the hole
grew large enough to give rise to significant UV increases
in southern Chile, and cataracts and malignant melanomas take many
years to develop. To be sure, people do get sunburns and
skin cancer even in Alaska and northern Europe, and all
else being equal one expects on purely statistical grounds such
cases to increase, from a small number to a slightly larger number.
All else is definitely not equal, however - the residents are now
intensely aware of the hazards of UV radiation and are likely to
protect themselves better. I suspect that the increase in
sun-related skin problems noted by the dermatologists comes about
because more people are taking such cases to their doctors.

As for the blind sheep, a group at Johns Hopkins has investigated
this and ascribes it to a local infection ("pink eye"). [Pearce]

This is not meant to dismiss UV-B increases in Patagonia as
insignificant. Damage to local plants, for example, may well emerge
in the long term, as the ozone hole is expected to last for 50
years or more. The biological consequences of UV radiation are real,
but often very subtle; I personally find it hard to believe that
such effects are showing up so soon, and in such a dramatic fashion.
Ozone depletion is a real problem, but this particular story is a red
herring.

8. What effects does increased UV have upon plant life?

Generally harmful, but hard to quantify. Many experiments have
studied the response of plants to UV-B radiation, either by
irradiating the plants directly or by filtering out some of the UV
in a low-latitude environment where it is naturally high. The
artificial UV sources do not have the same spectrum as solar
radiation, however, while the filtering experiments do not
necessarily isolate all of the variables, even when climate
and humidity are controlled by growing the plants in a greenhouse.

 Out of some 200 agricultural plants tested, more than half show
sensitivity to UV-B increases. The measured effects vary markedly
from one species to another; some adapt very readily while others are
seriously damaged. Even within species there are marked differences;

for example, one soybean variety showed a 25% growth reduction under a simulated ozone depletion of 16%, whereas another variety showed no significant yield reduction. The general sense seems to be that ozone depletion amounting to 10% or more could seriously affect agriculture. Smaller depletions could have a severe impact on local ecosystems, but very little is known about this at present.

I have not investigated the literature on this in detail, not being a biologist. Interested readers should consult [Tevini and Teramura] or the book by [Tevini] and the references therein. If any botanist out there would like to write a summary for this FAQ, please let me know.

9. What effects does increased UV have on marine life?

Again, generally harmful but hard to quantify. Seawater is surprisingly transparent to UV-B. In clear waters radiation at 315 nm is attenuated by only 14% per meter depth. [Jerlov]. Many marine creatures live in surface waters, and they have evolved a variety of methods to cope with UV. Some simply swim to lower depths, some develop protective coatings, some work at night to repair the damage done during the day. These natural mechanisms however, are often triggered by visible light intensities, in which case they do not protect against an increase in the ratio of UV to visible light. Also, if a photosynthesizing organism protects itself by staying at lower depths, it will get less visible light and produce less oxygen. An increase in UV-B can thus affect an ecosystem without necessarily killing off individual organisms.

Many experiments have been carried out to determine the response of various marine creatures to UV radiation; as with land plants the effects vary a great deal from one species to another, and it is difficult to draw general conclusions at this stage. We can infer that organisms that live in tropical waters are safe, since there is little or no ozone depletion there, and that organisms that are capable of living in the tropics are probably safe from large depletions at high latitudes since UV intensities at high latitudes are always low. (One must be a little careful with the second inference if the organism's natural defenses are stimulated by visible light.) The problems arise with organisms

that have adapted to the naturally low UV levels of polar regions.

In this case, we have a natural laboratory for studying UV effects: the Antarctic Ozone hole. (Part III of the FAQ discusses the hole in detail.) The outer parts of the hole extend far out into the ocean, beyond the pack ice, and these waters get springtime UV-B doses equal to or greater than what is seen in a normal antarctic summer. [Frederick and Alberts] [Smith et al.]. The UV in shallow surface waters is effectively even higher, because the sea ice is more transparent in spring than in summer. There has been speculation that this UV could cause a population collapse in the marine phytoplankton, the microscopic plants that comprise the base of the food chain.

To my knowledge, only one field study has been published so far. [Smith et al.]. These workers measured the photosynthetic productivity of the phytoplankton in the "marginal ice zone" (MIZ), the layer of relatively fresh meltwater that lies over saltier deep water. Since the outer boundary of the ozone hole is relatively sharp and fluctuates from day to day, they were able to compare photosynthesis inside and outside the hole, and to correlate photosynthetic yield with shipboard UV measurements. They concluded that the UV-B increase brought about an overall decrease of 6-12% in phytoplankton productivity. Since the "hole" lasts for about 10-12 weeks, this corresponds to an overall decrease of 2-4% for the year. The natural variability in phytoplankton productivity from year to year is estimated to be about + or - 25%, so the immediate effects of the ozone hole, while real, are far from catastrophic. To quote from [Smith et al.]: "Our estimated loss of 7 x 10^12 g of carbon per year is about three orders of magnitude smaller than estimates of global phytoplankton production and thus is not likely to be significant in this context. On the other hand, we find that the O3-induced loss to a natural community of phytoplankton in the MIZ is measurable and the subsequent ecological consequences of the magnitude and timing of this early spring loss remain to be determined." It appears, then, that overall loss in productivity is not large - yet. (The cumulative effects on the marine community are not known. The ozone hole first became large enough to expose marine life to large UV increases in 1987, and [Smith et al.] carried out their survey in 1990.) Ecological consequences - the displacement of UV-sensitive

species by UV-tolerant ones - are likely to be more important than a decline in overall productivity, although they are poorly understood at present.

10. Is UV-B responsible for the amphibian decline?

[This is a temporary answer, included essentially as a pointer to the paper by Blaustein et al. I intend to include a more substantive paragraph in the April 1994 version of this FAQ, after I have had a chance to look over the literature. Please send information and comments to rparson@rintintin.colorado.edu]

UV-B is unlikely to be the primary cause of this mysterious phenomenon, but it may be one of several interacting factors [Wake]. A recent field study [Blaustein et al.] in the Oregon Cascades found that the eggs of two species of frogs that are known to be in serious decline are adversely affected by ambient levels of UV-B, while another species that is not in decline seems to be unaffected.

REFERENCES FOR PART IV

A remark on references: they are neither representative nor comprehensive. There are hundreds of people working on these problems. For the most part I have limited myself to papers that are (1) widely available (if possible, Science or Nature rather than archival journals such as J. Geophys. Res.) and (2) directly related to the "frequently asked questions". Readers who want to see "who did what" should consult the review articles listed below, or, if they can get them, the WMO reports which are extensively documented.

Introductory Reading:

[Graedel and Crutzen] T. E. Graedel and P. J. Crutzen, Atmospheric Change: an Earth System Perspective, Freeman, NY 1993.

[Rowland 1989] F. S. Rowland, "Chlorofluorocarbons and the

depletion of stratospheric ozone", American Scientist 77, 36, 1989.

[Zurer] P. S. Zurer, "Ozone Depletion's Recurring Surprises Challenge Atmospheric Scientists", Chemical and Engineering News, 24 May 1993, pp. 9-18.

Books and Review Articles:

[Rowland 1991] F. S. Rowland, "Stratospheric Ozone Depletion", Ann. Rev. Phys. Chem. 42, 731, 1991.

[Tevini] M. Tevini, editor: "UV-B Radiation and Ozone Depletion: Effects on humans, animals, plants, microorganisms, and materials" Lewis Publishers, Boca Raton, 1993.

[Wayne] R. P. Wayne, Chemistry of Atmospheres, 2nd. Ed.,
 Oxford, 1991.

[WMO 1988] World Meteorological Organization,
Report of the International Ozone Trends Panel,
 Global Ozone Research and Monitoring Project - Report #18.

[WMO 1989] World Meteorological Organization,
Scientific Assessment of Stratospheric Ozone: 1989
 Global Ozone Research and Monitoring Project - Report #20.

[WMO 1991] World Meteorological Organization,
Scientific Assessment of Ozone Depletion: 1991
 Global Ozone Research and Monitoring Project - Report #25.

More Specialized:

[Blaustein et al.] A. R. Blaustein, P. D. Hoffman, D. G. Hokit, J. M. Kiesecker, S. C. Walls, and J. B. Hays, "UV repair and resistance to solar UV-B in amphibian eggs: A link to population declines?", Proc. Nat. Acad. Sci. 91, 1791, 1994.

[Blumthaler and Ambach] M. Blumthaler and W. Ambach, "Indication of

increasing solar ultraviolet-B radiation flux in alpine regions",
Science 248, 206, 1990.

[Bruehl and Crutzen] C. Bruehl and P. Crutzen, "On the
disproportionate role of tropospheric ozone as a filter against
solar UV-B radiation",Geophys. Res. Lett. 16, 703, 1989.

[Frederick and Alberts] J.E. Frederick and A. Alberts, "Prolonged
 enhancement in surface ultraviolet radiation during the Antarctic
 spring of 1990", Geophys. Res. Lett. 18, 1869, 1991.

[Frederick et al. 1993] J.E. Frederick, P.F. Soulen, S.B. Diaz,
I. Smolskaia, C.R. Booth, T. Lucas, and D. Neuschuler,
"Solar Ultraviolet Irradiance Observed from Southern Argentina:
 September 1990 to March 1991", J. Geophys. Res. 98, 8891, 1993.

[Grant] W. Grant, "Global stratospheric ozone and UV-B radiation",
  Science 242, 1111, 1988. (a comment on [Scotto et al.])

[Jerlov] N.G. Jerlov, "Ultraviolet Radiation in the Sea",
Nature 166, 112, 1950.

[Kerr and McElroy] J. B. Kerr and C. T. McElroy, "Evidence for Large
 Upward Trends of Ultraviolet-B Radiation Linked to Ozone Depletion",
 Science 262, 1032, 1993.

[Liu et al.] S.C. Liu, S.A. McKeen, and S. Madronich, "Effect of
 anthropogenic aerosols on biologically active ultraviolet
radiation", Geophys. Res. Lett. 18, 2265, 1991.

[Madronich 1992] S. Madronich, "Implications of recent total
atmospheric ozone measurements for biologically active ultraviolet
radiation reaching the earth's surface",
Geophys. Res. Lett. 19, 37, 1992.

[Madronich 1993] S. Madronich, in [Tevini], above.

[Madronich and de Gruiji] S. Madronich and F. R. de Gruiji,
"Skin Cancer and UV radiation", Nature 366, 23, 1993.

[Pearce] F. Pearce, "Ozone hole 'innocent' of Chile's ills",

New Scientist #1887, 7, 21 Aug. 1993.

[Roach] M. Roach, "Sun Struck", Health, May/June 1992, p. 41.
 (See especially the sidebar by Steven Finch on p. 50).

[Scotto et al.] J. Scotto, G. Cotton, F. Urbach, D. Berger, and T.
Fears, "Biologically effective ultraviolet radiation: surface
measurements in the U.S.", Science 239, 762, 1988.

[Seckmeyer and McKenzie] G. Seckmeyer and R. L. McKenzie,
"Increased ultraviolet radiation in New Zealand (45 degrees S)
relative to Germany (48 degrees N.)", Nature 359, 135, 1992.

[Setlow et al.] R. B. Setlow, E. Grist, K. Thompson and
A. D. Woodhead, "Wavelengths effective in induction of Malignant
Melanoma", PNAS 90, 6666, 1993.

[Skolnick] A. Skolnick, "Is ozone loss to blame for melanoma
upsurge?" JAMA, 265, 3218, June 26 1991.

[Smith et al.] R. Smith, B. Prezelin, K. Baker, R. Bidigare, N.
Boucher, T. Coley, D. Karentz, S. MacIntyre, H. Matlick, D.
Menzies, M. Ondrusek, Z. Wan, and K. Waters, "Ozone depletion:
Ultraviolet radiation and phytoplankton biology in antarctic
waters", Science 255, 952, 1992.

[Tevini and Teramura] M. Tevini and A. H. Teramura, "UV-B effects
on terrestrial plants", Photochemistry and Photobiology, 50,
479, 1989. (This issue contains a number of other papers dealing
with biological effects of UV-B radiation.)

[Wake] D. B. Wake, "Declining Amphibian Populations", Science
 253, 860, 1991.